STUDIES ON THE KINETICS AND MECHANISM OF THE OXIDATION OF CARBOHYDRATES IN THE ABSENCE AND PRESENCE OF SURFACTANTS

ABSTRACT
THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

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ABSTRACT

Carbohydrates are widely distributed in plants and animals, where they fulfill both structural and metabolic roles. They are of three types, namely, mono–, oligo–, and polysaccharides. Monosaccharides are fundamental biomolecules in that they are building blocks of polysaccharides. They are building blocks of nucleotides also and, hence, of nucleic acids and of the chemical ADP/ATP energy storage system.

Oxidation and reduction reactions of sugars play key roles in biochemistry. Oxidation of sugars provides energy for organisms to carry out their life processes. The physiological and microbiological activities of carbohydrates depend largely in their redox behavior. Oxidation of monosaccharides by different oxidizing agents are, therefore, of special importance due to their biological relevance.[1–4] Due to multihydroxy functionality of saccharides they can chelate and coordinate to many metal ions. Cerium(IV) is used as an oxidant not only in analysis, but also in synthetic organic chemistry. Kinetic and mechanistic aspects of cerium(IV) oxidation of monosaccharides has also been studied[1,5–10] but no attempt has been made on such redox systems in presence of micelles.

The chemical approach to biological problems through investigations of models rests upon the ability of the chosen system to mimic some functions of the biological ensemble. Surfactants in aqueous media have been extensively used as model systems. Surfactants are amphipathic molecules which have distinct hydrophobic and hydrophilic regions. Over a narrow concentration

range, defined as the critical micelle concentration, or cmc, surfactants dynamically associate to form large molecular aggregates, called micelles.

Rates of numerous organic and inorganic reactions are affected by micelles in aqueous solutions.[11] Catalysis or inhibition is the consequence of substrate solubilization in the micellar pseudophase. Rate effects can be attributed to electrostatic, hydrophobic, electrophilic and/or nucleophilic interactions with the resultant alteration of free energy of activation for the overall process. Interest in micellar chemistry has been prompted by the proposed similarities between the structures of the globular proteins and spherical micelles and between micellar and enzymatic catalyses.

Therefore, the present thesis entitled **'Studies on the Kinetics and Mechanism of the Oxidation of Carbohydrates in the Absence and Presence of Surfactants'** is exclusively devoted to study the role of cationic and anionic micelles on reaction of cerium(IV) and carbohydrates. The surfactants used in this study are CTAB (cationic) and SDS (anionic) and the carbohydrates are two aldopentoses (D(+)xylose and L(+)arabinose), two aldohexoses (D(+)glucose and D(+)mannose), and two ketohexoses (D(–)fructose and L(–)sorbose). There are three chapters in the thesis, namely (i) Chapter 1 – **Introduction**; (ii) Chapter 2 – **Experimental**; and (iii) Chapter 3 – **Results and Discussion**.

Chapter 1 includes introduction about carbohydrates, their importance, properties, chelating ability and reactivity towards metal ions, especially with cerium(IV). A brief account of the kinetics and mechanism of the cerium(IV)—carbohydrate reactions studied by different workers is also given.

The classification of surfactants, their uses, behavior and the pseudophase model and its applicability to the micellar catalyzed reactions is also provided. The chapter ends with the statement of the problem which suggests the importance of this study.

All the experimental details are described in **Chapter 2**. The materials used, their structure and formulas, sources and purities are given along with the method for the preparation of solutions and kinetic measurements. The method of cmc determination and procedure for the characterization and identification of products and stoichiometric determinations are also detailed in this chapter. Cerium(IV) is reduced to cerium(III), which is colorless at the maximum wavelength of cerium(IV), *i.e.,* 385nm. Therefore, examples of the spectra of the reaction product are also given in **Chapter 2**.

Chapter 3 – Results and Discussion, as the name implies, covers all the results obtained with their discussion. The oxidative degradation of carbohydrates by cerium(IV) has been found to be slow in aqueous H_2SO_4 medium with the evidence of autocatalysis. The effect of varying the concentrations of cerium(IV), carbohydrate, sulfuric acid, SO_4^{2-}, HSO_4^- and surfactant was seen to elaborate their role in the cerium(IV)—carbohydrate redox reactions. The values of pseudo-first-order rate constants were independent on the initial concentrations of oxidant (cerium(IV)) indicating the first-order dependence of the reaction rate on [Ce(IV)]. The plots of rate constants *versus* [reductant] were linear with zero intercepts, clearly suggesting the first-order dependence of rate constants on carbohydrates. The pseudo-first-

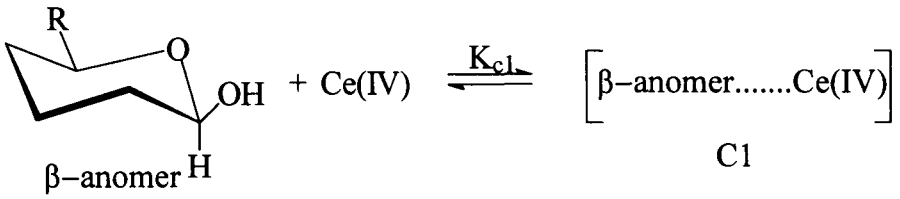
order rate constants decreased with increase in concentrations of H_2SO_4 and HSO_4^- while a rate increase was found with increase in $[SO_4^{2-}]$. Effect of temperature on the reaction rate was studied to obtain the values of thermodynamic parameters. As regards the effect of surfactants, the rate constants increased as the concentration of cationic CTAB increased whereas anionic SDS has no effect (which may be due to the electrostatic repulsion between the negative head group of SDS and the reactive species of cerium(IV)). Lower values of activation energies for the reactions in CTAB medium as compared to aqueous medium confirm the catalysis.

Existence of various forms of monosaccharides and cerium(IV) has been discussed and β-anomer of pyranoid form is envisaged to be involved in the oxidation of monosaccharides. The rate increasing effect of CTAB and constancy of rates on varying [SDS] showed the participation of negatively charged species of cerium(IV). On the basis of $[H_2SO_4]$ and $[HSO_4^-]$–dependencies, species $Ce(SO_4)_3^{2-}$ and/or $HCe(SO_4)_3^-$ are proposed as the reactive species.

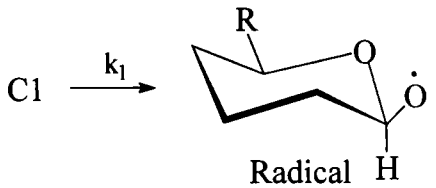
A probable mechanism is presented and discussed. The reactions start with formation of a complex between cerium(IV) and carbohydrate which undergoes decomposition in rate determining step. The oxidation products of the reactions are Ce(III), lactones, and aldonic acids (aldoses)/formaldehyde (ketoses).

The Mechanism for

(A) Aldoses



(1)



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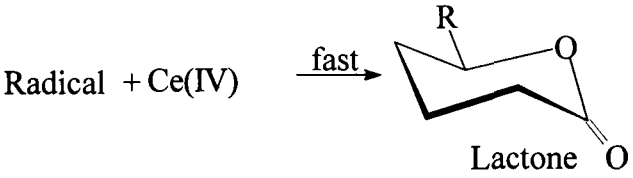

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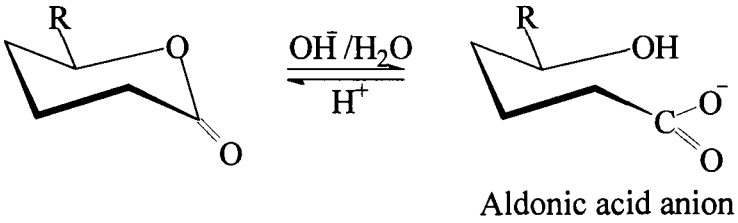
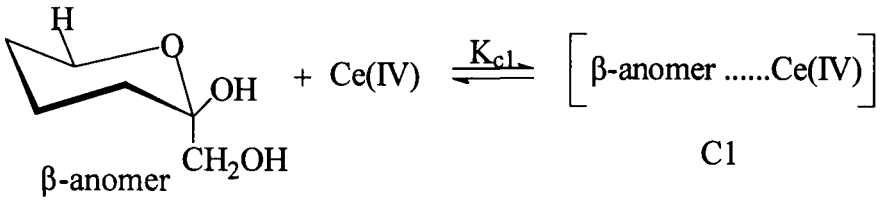


(4)

(R = —H (for aldopentoses) or $-CH_2OH$ (for aldohexoses) and Ce(IV) denotes the kinetically active Ce(IV)–species)

(B) Ketoses



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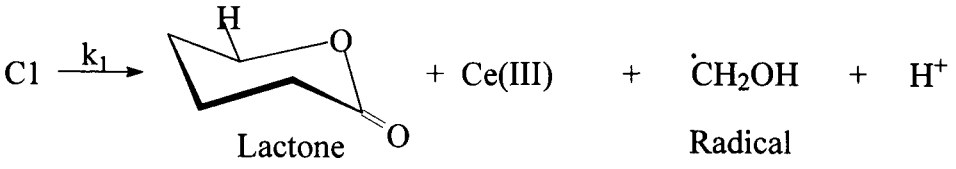
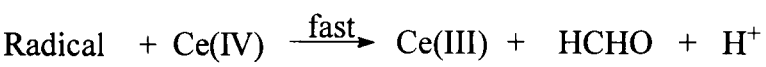


(6)



(7)

Effect of the variables [oxidant], [reductant], [H_2SO_4], and temperature were also studied in presence of CTAB and it was found that the dependence of rate constants on all variables was same as in case of aqueous medium. Thus, the same mechanism operative in the aqueous medium is being followed in the CTAB micellar medium too.

The CTAB micelle-catalyzed kinetic results are interpreted by the Menger–Portnoy[12] model where cerium(IV) in water associates with micellized surfactant (D_n) giving micellized cerium(IV) and the reaction occurring in the aqueous and micellar pseudophases with first-order rate constants (k'_w and k'_m). The first-order rate constant for the overall reaction (k_Ψ) is given by the following equation

$$k_\Psi = \frac{k'_w + k'_m K_s [D_n]}{1 + K_s [D_n]} \qquad (8)$$

which, on rearrangement gives

$$\frac{1}{(k'_w - k_\Psi)} = \frac{1}{(k'_w - k'_m)} + \frac{1}{(k'_w - k'_m) K_s [D_n]} \qquad (9)$$

The values of k'_m and K_s were evaluated from the slopes and intercepts of the plots of $1/(k'_w - k_\Psi)$ *versus* $1/[D_n]$.

The positive catalytic effect of CTAB micelles on the Ce(IV)–carbohydrate redox reactions has been explained in the following manner. The chemically active anionic Ce(IV)–species gets associated with the cationic micelles. The second reactant, carbohydrate, has no hydrophobicity due to the

presence of hydrophilic —OH groups. As the reaction proceeds through the formation of a complex (see Eq. (1)/(5)), the associated Ce(IV)–species may form complex C1 at the Stern and Gouy-Chapman layers' junctural region. The complex may now orient in a manner suitable for continuing the reaction. A possible arrangement (although highly schematic) could be as shown in Fig. 1.

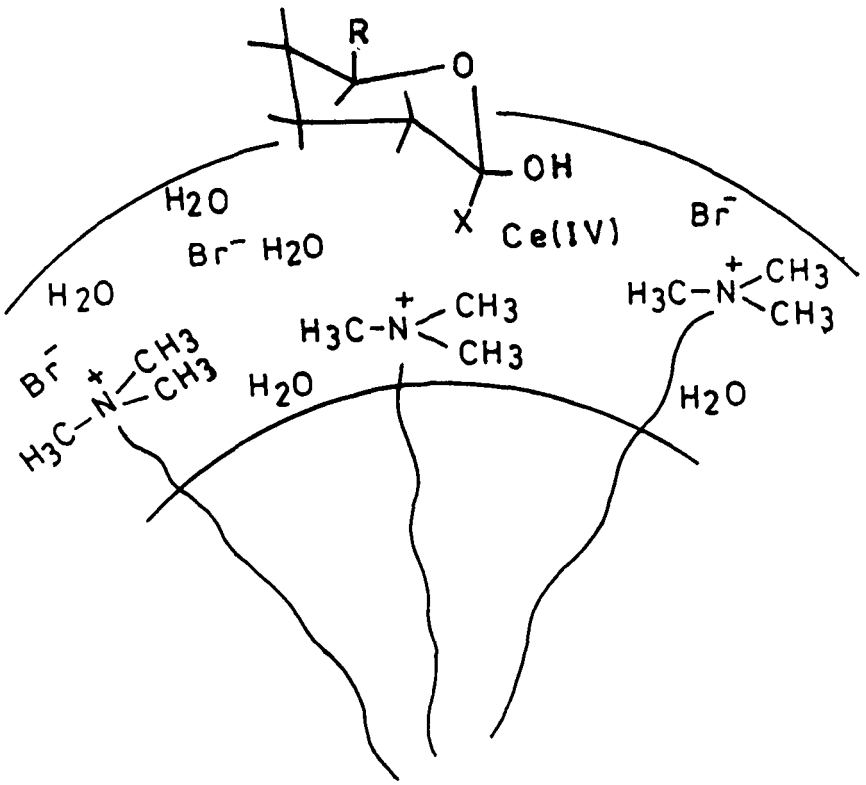


Fig. 1: Schematic model showing probable location of reactants for the ionic micellar catalyzed redox reaction between cerium(IV) and carbohydrates.

Added inorganic salts (Na_2SO_4, $NaNO_3$, NaCl) inhibit the CTAB-catalyzed reaction that may be due to the exclusion of reactive species of cerium(IV) from the reaction site. The inhibitory power increases in the order $Cl^- < NO_3^- < SO_4^{2-}$.

On the basis of the second –order rate constant values for the reactivity of carbohydrates with cerium(IV), it is inferred that presence of —OH, —CHO and ketonic groups increase the reducing power in the order aldohexoses < aldopentoses < ketohexoses. The trend shows that the oxidation by cerium(IV) seemingly depends on the number of —OH groups, stereochemistry and the chelating ability of the monosaccharides. D(–)fructose has greater tendency to reduce cerium(IV) in comparison to L-sorbose and other monosaccharides (L(–)sorbose > L(+)arabinose > D(+)xylose > D(+)mannose > D(+)glucose). It is interesting to note that the oxidation rates of various monosaccharides studied are of the same order. This means that these sugars are oxidized by a common mechanism, *i.e.*, cerium forming a complex with C-1 hydroxyl group of the sugar prior to its rate-limiting disproportionation to a free radical.

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To
My Parents

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Certificate

This is to certify that the thesis entitled "**Studies on the Kinetics and Mechanism of the Oxidation of Carbohydrates in the Absence and Presence of Surfactants**" is the original work carried out by **Mr. Mohd. Sajid Ali** under my supervision and is suitable for submission for the award of Ph.D. degree in **Chemistry**.

(Prof. Kabir-ud-Din)

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Sajid Ali

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List of Publications

1. Effect of anionic and cationic micelles on the oxidation of D-glucose by cerium(IV) in presence of H_2SO_4
   Kabir-ud-Din, **Mohd. Sajid Ali**, Zaheer Khan
   Colloid Polym. Sci., 2005, **284**, 10-18.

2. Oxidation of L(+)arabinose by cerium(IV) in presence of anionic and cationic micelles.
   Kabir-ud-Din, **Mohd. Sajid Ali**, Zaheer Khan
   Indian J. Chem., 2005, **44A**, 2462-2469.

3. Effect of surfactant micelles on the kinetics of oxidation of D-fructose by cerium(IV) in sulfuric acid medium.
   Kabir-ud-Din, **Mohd. Sajid Ali**, Zaheer Khan
   Int. J. Chem. Kinet., 2006, **38**, 18-25.

4. Kinetics of the oxidative degradation of D-xylose in presence and absence of cationic and anionic surfactants.
   Kabir-ud-Din, **Mohd. Sajid Ali**, Zaheer Khan
   Colloid Polym. Sci., 2006, **284**, 627-633.

5. Micelle-assisted cerium(IV) oxidation of L-sorbose in aqueous sulfuric acid.
   Kabir-ud-Din, **Mohd. Sajid Ali**, Zaheer Khan
   Int. J. Chem. Kinet., (Revised manuscript submitted).

6. Micelle catalyzed oxidation of D-mannose by cerium(IV) in sulfuric acid.
   Kabir-ud-Din, **Mohd. Sajid Ali**, Zaheer Khan
   Inorg. React. Mech., (Communicated).

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CHAPTER 1

INTRODUCTION

A. Oxidation of Carbohydrates

The simple organic compounds from which living organisms are constructed are unique to life and do not otherwise occur on the earth today, except as products of biological activity. These building-block compounds, called biomolecules, were selected during the course of biological evolution for their fitness in performing specific cell functions. They are identical in all organisms. Biomolecules are related to each other and interact in a kind of molecular "game" or logic. The size, shape and chemical reactivity of biomolecules enable them not only to serve as building blocks of the intricate structure of cells, but also to participate in their dynamic, self-sustaining transformation of energy and matter. Biomolecules must therefore be examined from two viewpoints, that of the chemist and that of the biologist.

Living things are composed of lifeless molecules. When these molecules are isolated and examined individually, they conform to all the physical and chemical laws that describe the behavior of inanimate matter.

Carbohydrates are one of the four major classes of biomolecules along with proteins, nucleic acids, and lipids. Carbohydrates are aldehyde or ketone compounds with multiple hydroxyl groups which may be classified as monosaccharides, oligosaccharides, and polysaccharides; the term saccharide is derived from the Greek word for sugar. Monosaccharides are single polyhydroxyaldehyde (known as aldoses, *e.g.*, glucose) or polyhydroxyketone

units (known as ketoses, *e.g.*, fructose), whereas oligosaccharides consist of two to ten monosaccharide units joined together by glycosidic linkages. Sucrose and lactose are disaccharides, since they are each made up of two monosaccharide units. Polysaccharides, as the name implies, may contain hundreds of monosaccharide units.

Carbohydrates make up most of the organic matter on earth because of their extensive roles in all forms of life. Carbohydrates serve as energy stores, fuels, and metabolic intermediates. Ribose and deoxyribose sugars form part of the structural framework of RNA and DNA. Carbohydrates are linked to many proteins (glycoproteins) and lipids (glycolipids), where they play key role in mediating interactions among cells and interaction between cells and other elements in cellular environment.

Carbohydrates provide the skeletal framework for tissues and organs of the human body and serve as lubricants and support elements of connective tissue. Major energy requirements of the body are met by dietary carbohydrates. They confer biological specificity and provide recognition elements on cell membranes.

Carbohydrates form the most abundant group of the natural products and are found in all classes of living organisms.[1–8] They serve as a direct link between the energy of the sun and metabolic energy that is required to sustain life. In organisms, capable of photosynthesis, solar energy is harvested to derive reaction in which glucose is synthesized from carbon dioxide and water. The

energy stored in "carbon fixation" process then gradually moves upwards into the food chain. The living organisms that partake the products of photosynthesis obtain useful energy by oxidizing the carbohydrates back into carbon dioxide and water through the process of glycolysis and respiration.

In addition to their pivotal role in metabolism, carbohydrates also play an important role in many organisms. Some examples of the latter type include cellulose, chitin, lipopolysaccharide, and the bacterial murein, all of which are derived from repeating sugar units which may have additional cross-linking components for rigidity. Furthermore, many biotic secondary metabolites such as cardioglycosides, macrolide antibiotics, and aminoglycoside antibiotics rely on the sugar components for solubility and activity. In addition, carbohydrates are used as convenient precursors for the biosynthesis of other important building blocks such as aromatic amino acids. Carbohydrates also have many applications in industrial processes. For example, the food industry uses sucrose as a sweetening agent, a preservative, and a raw material for fermentation. Starch is used as a raw material for the manufacture of many goods. Cotton is still one of the most popular fabrics and an important raw material for the textile industry. Paper and other derivatives of cellulose are important for the manufacture of packaging materials and plastics.

Glycosides are compounds formed from a condensation between a monosaccharide, or monosaccharide residue, and the hydroxyl group of the

second residue that may, or may not be another monosaccharide. Glycosides are found in many drugs and spices and in the constituents of animal tissues.

A knowledge of the structure and properties of the carbohydrates of physiologic significance is essential to understanding their fundamental role in the economy of the mammalian organism. The sugar glucose is the most important carbohydrate. It is as glucose that the bulk of dietary carbohydrate is absorbed into the bloodstream or into which it is converted in the liver, and it is from glucose that all other carbohydrates in the body can be formed.

Carbohydrates exert a wide range of functions in living organisms, and due to the wide distribution of metals and their complex functions for all forms of life, metal-carbohydrate interactions are a key for understanding bioinorganic chemistry, and the study of complexation of carbohydrates to metals is one of the main objectives of carbohydrate coordination chemistry. Metal complexes of natural carbohydrates have been attracting interest for many years because these compounds participate in vitally important processes; they are used for configurational and conformational analysis, determination, and separation of sugars. Many carbohydrates easily undergo redox processes. Facile oxidation can abrogate metal binding, particularly so with high oxidation state transition metals.

The physiological and microbiological activities of carbohydrates depend largely in their redox behavior. Oxidation of monosaccharides by different oxidizing agents are, therefore, of special importance due to their biological

relevance.[9-12] Due to multihydroxy functionality of saccharides they can chelate and coordinate to many metal ions. Besides acting simply as effective chelators,[13] in many cases they are also reducing agents, *e.g.*, for metal ions such as Ce(IV),[9] Fe(III),[10] Co(III),[11] V(V),[14] depending on the acidity of the medium.

B. Cerium(IV) Oxidation of Carbohydrates

In plant and animal tissues cerium is an important metal element,[15] it combines with most of pivotal living active molecules and plays important physiological function. Cerium(III), the reduction product of cerium(IV), with suited concentration can activate plant growth and improve the metabolism level of sugar and grease. For this reason, various fertilizers and fodder containing cerium(III) are widely applied in China.

Cerium(IV) has been used as an oxidizing agent and an analytical reagent, especially in an acid medium.[16] Oxidation of organic compounds with cerium(IV) are potentially interesting since cerium(IV) is an unusually strong, one-electron oxidant. Moreover, unique reactions of cerium(IV) with organic compounds can be expected because of specific coordination properties of the ion with various organic and inorganic ligands.

The oxidation of organic substances by cerium(IV) reagents is found to follow different mechanisms, depending on the type of acid media used. The oxidation potential of the Ce(IV)- Ce(III) couple is markedly ligand dependent, *e.g.* the potentials are 1.70 to 1.71, 1.61, 1.44, and 1.28 volts in 1N perchloric,

nitric, sulfuric, and hydrochloric acids, respectively.[17–21] The oxidation potential in hydrochloric acid is probably low (in negative sense), because reaction at the platinum electrode is not reversible.[22] Increasing the acid concentration from 1N to 8N increases the potential in perchloric acid to 1.87 volts, whereas a decrease to 1.56 and 1.42 volts is observed, respectively, in nitric and sulfuric acids.[17,18] The increase in potential with increasing perchloric acid concentration is in part attributed to cerium(IV) hydrolysis products. The decrease in potential in sulfuric acid and nitric acid with increasing acid concentration can be attributed to complexing of cerium ions with sulfate and nitrate anions. These predictions have been verified quantitatively for perchloric and sulfuric acid solutions. The standard potential (E°) in sulfuric acid was calculated to be 1.74 volts[22] when account was made for bisulfate dissociation and the equilibria (Eqs. (1.1)–(1.3)):

$$Ce(IV) + HSO_4^- \rightleftharpoons Ce(SO_4)^{2+} + H^+ \qquad K_1 = 3500 \qquad (1.1)^{23}$$

$$Ce(SO_4)^{2+} + HSO_4^- \rightleftharpoons Ce(SO_4)_2 + H^+ \qquad K_2 = 200 \qquad (1.2)^{23}$$

$$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons Ce(SO_4)_3^{2-} + H^+ \qquad K_3 = 20 \qquad (1.3)^{23}$$

Scheme 1.1

As regards equilibria in the aqueous H_2SO_4 media, the studies by Hardwick and Robertson[23] are very important, but later on Bugaenko and Kuan-Lin[24] have modified the observation made by Hardwick and Robertson who proposed the tri-sulfato species as $Ce(SO_4)_3^{2-}$. From the studies of Bugaenko and Kuan-Lin, it was established that the tri-sulfato species is $HCe(SO_4)_3^-$.

According to their studies[24] in aqueous H_2SO_4 media (up to *ca.* 2 mol dm^{-3}) the predominant equilibria are represented by Eqs. (1.1), (1.2), (1.4), and (1.5):

$$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons HCe(SO_4)_3^- \qquad K_5 = 0.6 \pm 0.1 \qquad (1.4)^{24}$$

$$HCe(SO_4)_3^- + H_2SO_4 \rightleftharpoons H_3Ce(SO_4)_4^- \qquad K_6 = 2 \pm 1 \qquad (1.5)^{24}$$

Scheme 1.2

At higher concentrations of H_2SO_4, the concentration of the $H_3Ce(SO_4)_4^-$ species increases gradually where a new species $H_4Ce(SO_4)_4$ has also been suggested.[25] Due to complexation in aqueous H_2SO_4 media, the tendency of cerium(IV) species to undergo hydrolysis is remarkably suppressed, but in aqueous $HClO_4$ media, hydrolysis leads to $Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$ which further undergo dimerization producing $CeOCe^{6+}$.[26]

The cerium(IV) equilibria are important in interpreting oxidation of organic compounds. Kinetic and additional spectral measurements also indicate that the degree of ceric perchlorate association depends on acid concentration.[27–29] However, a monomer–dimer equilibrium may be an oversimplification, since above pH 0.7 colloidal polymers slowly form.[30] Ceric nitrate equilibria are complicated by dimerization, hydrolysis, and association with cerium(III).[31,32] This could provide an added complexity in cerium(IV) oxidations where appreciable quantities of cerium(III) are formed.

A good number of studies of the kinetics and mechanism of the oxidation of a variety of organic substrates have been made by cerium(IV) either in sulfuric acid or perchloric acid medium.[16,33,34] Oxidation of carbohydrates by cerium(IV) has also been a subject of interest,[9,35–53] especially to find out if the same mechanism is operative in this case, too, as it operates in the case of alcohols, glycols, formaldehyde, *etc.*

Mehrotra[35,38] investigated the degradation of aldoses by cerium(IV) sulfate in aqueous sulfuric acid. Pottenger and Johnson[36] studied the mechanism of cerium(IV) oxidation of glucose and cellulose in 1 mol dm^{-3} perchloric acid. The oxidation of D-glucose,[36,38,40] D-galactose,[42] L-arabinose,[42] and L-sorbose[43] by cerium(IV) has been studied, the reaction generally proceeded to give the corresponding lactones and aldonic acids.

Sala and coworkers[9,39] reported the oxidative decarboxylation of lactones by cerium(IV) for the synthesis of 2-deoxy-D-erythro-pentose and D-arabinose. Virtanen and coworkers[47] also studied the oxidation of various aldoses and ketoses by cerium(IV) in perchloric acid and reported the formation of two complexes in each case, one in pre-equilibrium reaction during mixing and other by the dissociation of first one. Sen Gupta *et al.*[49] investigated the oxidations of aldoses like D-ribose, D-erythrose, and DL-glyceraldehyde and compared the results obtained with that of D-glucose. The results showed that the oxidation of D-glucose, D-ribose, and D-erythrose by cerium(IV) were kinetically similar and DL-glyceraldehyde was oxidized by a different mechanism.

C. Surfactant and Surfactant Micelles

Interfaces are the boundary regions that separate different bulk regions of matter. They have special chemical, physical, and biological properties that have fascinated and drawn the attention of scientists from many different fields.[54] What makes the interface unique is the asymmetry in forces that is experienced by molecules and atomic species located there together with the almost two dimensional geometry of the interface. The chemical composition, the geometrical arrangement of the species, the equilibrium constants, pH, the motion of molecules, the thermodynamics and kinetics of ground- and excited-state chemical change, energy relaxation, and the phases and phase transitions of long chain amphiphilic monolayers are among the fundamental manifestations of the unique characteristics of an interface.[55] The study of chemical reactivity at liquid interfaces occupies an important place in chemistry.[56] Electron transfer, ion transfer, and proton transfer at the interfaces between two immiscible liquids are fundamentally important for understanding processes such as liquid chromatography, phase transfer catalysis,[57] drug delivery problems in pharmacology,[58] and other phenomena in membrane biophysics.[59] The uptake of pollutants by water clouds, an important atmospheric phenomenon,[60] involves reaction such as ionization at the water liquid/vapor interface.

A surfactant (a contraction of the term **surface active agent**) is a substance that when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a

marked degree the surface or interfacial free energies of the surfaces (or interfaces).[61]

Surfactants are compounds whose molecules are fitted with pronounced lipophilic and hydrophilic moieties; they are amphiphilic molecules. A process whereby dissolved surfactant molecules react to the repelling action of surrounding water is aggregation to form various kinds of supramolecular structures.[62]

A wide variety of surfactant compounds can be dispersed in aqueous solution to form organized assemblies, either by spontaneous combination or with the aid of sonication. Their formation can be rationalized in terms of hydrophobic–hydrophilic and electrostatic interactions,[63] as well as by thermodynamic considerations.[64,65] Interest in the biological function of some of these assemblies and unusual control of reactivity has prompted a number of structural studies of the different media.[66–72]

Surfactants find application in almost every chemical industry, including detergents, paints, dyestuffs, cosmetics, pharmaceuticals, agrochemicals, fibres, plastics. Moreover, surfactants play a major role in the oil industry, *e.g.*, in enhanced and tertiary oil recovery. They are also used for environmental protection, *e.g.*, in oil slick dispersants. Therefore, a fundamental understanding of the physical chemistry of surface active agents, their unusual properties, and their phase behavior is essential for most industrial chemists. In addition, an understanding of the basic phenomena involved in the application of surfactants,

such as in the preparation of emulsions and suspensions and their subsequent stabilization, in microemulsions, in wetting, spreading, and adhesion, *etc.*, is of vital importance in arriving at the right composition and control of the system involved. This is particularly the case with many formulations in chemical industry.[73]

Apart from the traditional use of surfactants, surfactant structures are increasingly being investigated as organic templates to synthesize mesoscopic inorganic materials with controlled nanoscale porosity, which are expected to have applications in electronics, optics, magnetism, and catalysis.[74]

Surfactants are also utilized in various biochemical methods, such as the purification and analysis of proteins, in analytical methods based on enzymes or immunological techniques, and in cleaning and regenerating chromatographic columns, biosensors, *etc*. Their ability to hinder protein adsorption is used, both to reduce the depletion of the substance that should be analyzed due to adsorption of the walls of test tubes, *etc.*,[75] and to hinder nonspecific adsorption of proteins in, *e.g.*, immunological methods and chromatography.[76]

General classification of surfactants

Numerous variations are possible within the structure of both the head and tail group of surfactants. The head group can be charged or neutral, small and compact in size, or a polymeric chain. The tail group is usually a single or

double, straight or branched hydrocarbon chain, but may also be a fluorocarbon, or siloxane, or contain aromatic group(s).

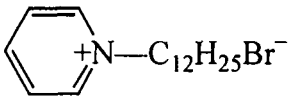
Since the hydrophilic part normally achieves its solubility either by ionic interactions or by hydrogen bonding, the simplest classification is based on surfactant head group type, with further subgroups according to the nature of the lyophobic moiety. Four basic classes therefore emerge as: the anionics and cationics (which dissociate in water into two oppositely charged species, *i.e.*, the surfactant ion and its counterion), the nonionics (include a highly polar (non charged) moiety, such as polyoxyethylene (—OCH_2CHO—) or polyol groups) and the zwitterionics or amphoterics (combine both as a positive and a negative group).

Examples:

(anionic)

$CH_3(CH_2)_{11}OSO_3^- Na^+$	$CH_3(CH_2)_{10}COO^- K^+$
sodium dodecyl sulfate	potassium laurate

(cationic)

$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$	
cetyltrimethylammonium-bromide	dodecylpyridinium bromide

(zwitterionic)

$C_{12}H_{25}N^{+}(CH_3)_2CH_2COO^{-}$	$CH_3(CH_2)_{11}N^{+}(CH_3)_2CH_2–CH_2–CH_2SO_3^{-}$
N-dodecyl-N:N-dimethyl-betaine	3-(dimethyldodecylammonio) propane-1-sulfonate

(nonionic)

$t–Oct–C_6H_4–(OCH_2CH_2)_xOH$	$C_9H_{19}C_6H_4(CH_2–CH_2–O–)_n—OH$
polyethyleneglycol-t-octyl-phenyl ether (x = 9 or 10)	nonyl phenyl-polyethylene glycol (n ~ 10)

Surfactants are key components of the organized assemblies used in biological systems. Nonionic surfactants based on carbohydrates are very important in biology. They have potential pharmaceutical (biocompatible formulations), biochemical (extraction of membrane proteins), and medicinal applications. Carbohydrate-based surfactants have water-soluble head group derived from a carbohydrate. This is linked by different functional groups to a hydrophobic part.

Surfactants have particular features that make them attractive in relation to chemical reactivity aspects and for large variety of applications. The application of surfactant based systems as drug delivery vehicles[77,78] is a growing research area that may develop further in the coming years. It is quite interesting that cationic amphiphiles are now widely used as an effective tool in delivering DNA into cells,[79,80] even mammalian cells.[81–85]

Bilayer-forming synthetic surfactants have been extensively used as membrane mimetic models, and some synthetic amphiphiles such as dihexadecyl phosphate or dioctadecylmethylammonium salts have found many different uses in strategic applied areas.[86]

Aqueous association colloids as reaction media offer alternatives to the use of organic solvents, and there is considerable interest in their use in water as reaction medium; they are attractive candidates in "green" chemistry.[87–91] For instance, Moss *et al.*[92,93] observed 1000- to 2000-fold rate enhancements in overall rate constants of hydrolysis of phosphates triesters catalyzed by different iodosocarboxylate ions of varying hydrophobicities in comicelles with CTACl and CTAOH.

Surfactant based reaction media have such kinds of features that make them useful in industrial-scale synthesis and interesting in developing "clean" processes. In fact, they are expected to be nontoxic and nonhazardous, they enhance reaction rates, reactions can usually be carried out under mild conditions, and in favorable cases surfactants can be separated and reused.

Surfactants alone or in combination with a wide variety of other ionic and non-ionic solutes, aggregate spontaneously and with a high degree of cooperativity in solution to form a variety of assemblies (or association colloids) whose structures depend both on solution composition and on the structures of components, primarily the surfactant.[63,94–96] All surfactant assemblies in homogeneous solution share an underlying organizational structure: a fluid,

hydrocarbon region separated from an aqueous region by an interfacial region with a thickness of the order of the diameter of the surfactant head group.

Largely depending on the molecular architecture of the amphiphile, a wealth of three-dimensional structures can be formed ranging from spherical and rod-like micelles to multilayer structures and to complex biological membranes, whose matrix is a lipid bilayer composed of phospholipids and glycolipids, incorporating proteins.[95,97,98] Ionic colloidal assemblies, *e.g.*, micelles, microemulsions, hemimicelles (solloids), bilayers, and vesicles are believed to be mimetic agents for membranes in biological systems. It has also been noted that, there are structural similarities between globular proteins and spherical micelles, and analogies between the catalytic effects of enzymes and functional micelles and between micellar catalysis and phase-transfer catalysis.[99–108] For these reasons, numerous investigators have focused attention on micelles and reactions in micellar media.

Micelles, micellar structure and properties

Normal micelles are assemblies of surfactants, which spontaneously aggregate (micellize) at concentrations greater than critical micelle concentration (cmc) in water and some associated solvents. Micelles are assumed to be spherical, with $\sim 10^2$ monomers, at low surfactant concentration, but they grow at high surfactant concentrations, especially with added electrolyte, and become rod-like. [94,106,109] The growth depends on the length of the hydrophobic group, the structure of the head group, and the added electrolyte. Simple rules

governing the packing of surfactant in micelles and similar assemblies have been proposed that relate the geometry of the assembly to the area of the head group and the length and volume of the hydrophobic residue.[95,110] The micellar core is oil like, and ionic or polar head groups at the surface are exposed to water.

Micelles have been investigated by an unusually wide variety of techniques including X-rays, nuclear magnetic resonance (NMR), electron spin resonance (ESR), fluorescence, static and dynamic light scattering, calorimetry, and kinetic probes.[111] Micellization is primarily driven by bulk hydrophobic interactions between the alkyl chains of the surfactant monomers and usually results from a favorable entropy change.[112] The overall Gibbs energy of the aggregate is a compromise of a complex set of interactions, with major contributions from head group repulsion and counterion binding (for ionic surfactants).[95] The residence times of individual surfactant molecule in the micelle are typically of the order of 10^{-5}–10^{-6} s, whereas the lifetime of the micellar entity is about 10^{-3}–10^{-1}s.

Ever since the discovery of micelles, theoretical models of micelle formation have in some way tried to account for the association–dissociation equilibrium that distinguishes micelles from other colloids. The earliest model is due to Hartley and regards the formation of a micelle as a chemical equilibrium between monomers, counterions and micelles. This model is the so–called Hartley micelle[113] and involves a hydrocarbon–like interior surrounded by polar or ionic head groups. The micelle is pictured as a roughly spherical aggregate

with a radius approximately corresponding to the extended length of the hydrocarbon chain of the surfactant (Fig. 1.1). Micellar head groups and associated counterions are fully hydrated and are found in the Stern layer. Some of the counterions are bound within the shear surface, and many are located in the Gouy-Chapman electrical double layer, where they are dissociated from micelle. This model has quite appropriately been dubbed the mass action (MA) approach.[114,115] The MA approach was followed by the phase separation (PS) model, advanced by Stainsby and Alexander in 1950,[116] wherein the micelles are treated as a phase separated from that containing the mesomeric species.

A good model is of Gruen, who has described a realistic model of a micelle[117,118] that involves a rather sharp interface between a dry hydrophobic hydrocarbon core and a region filled with surfactant head groups, some of the counterions, and water, namely the Stern region. This model has been validated using molecular dynamic simulations[119,120] and is valid for both ionic and nonionic micelles.

The overall structure of micelle is characterized by a situation in which the ionic and polar head groups reside at the surface of the aggregates, where they are in contact with water, with the alkyl chains in the interior of the micelle forming a relatively dry hydrophobic core.[121] The alkyl chains of micellized surfactant are not fully extended. Starting from the head group, the first two or three carbon–carbon bonds are usually *trans*, whereas *gauche* conformations are likely to be encountered near the centre of the chain. As a result, the terminal

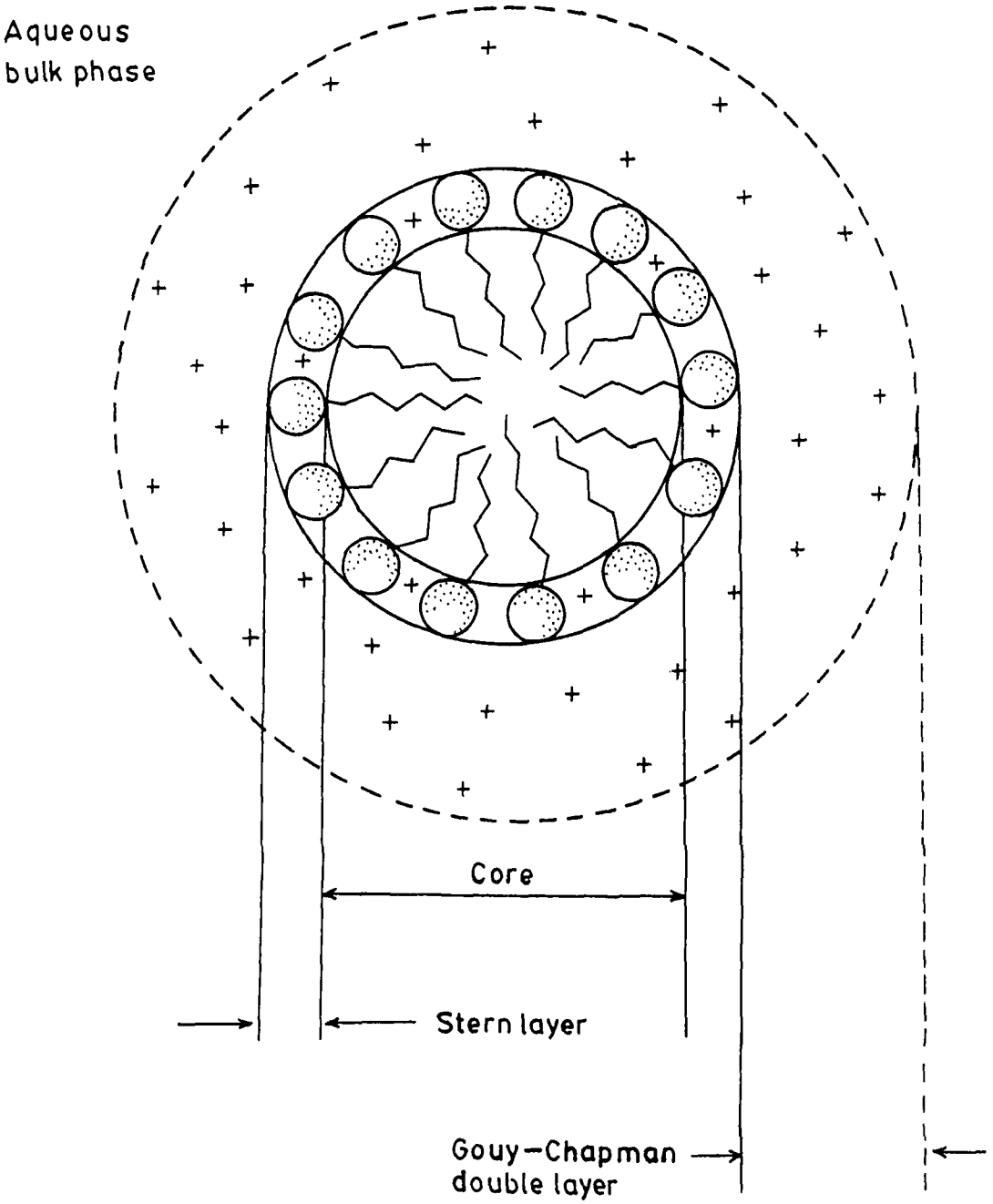


Fig. 1.1: Model of a typical ionic micelle showing the location of head groups (⊖), surfactant chains (/\/\/\) and the counterions (+).

methyl moieties of the chain can be located near the surface of the micelle and may even protrude into the aqueous medium.[122] Consequently, the micellar surface has a definite degree of hydrophobicity. NMR studies have shown that the hydrocarbon tails in a micelle are highly mobile and comparable in mobility to the chains in a liquid hydrocarbon.[123] The degree of water penetration into the micellar interior has long been a matter of debate. Small–angle neutron scattering studies have indicated that significant water penetration into the micellar core is unlikely.[124]

D. The Pseudophase Model

Kinetic studies in micellar systems have been in the scope of interest of many researchers for a longtime. The rates of enzymatic, organic, and inorganic reactions have been investigated in the presence of micelles by a great variety of surfactants. The chemical literature in the period 1900–1958 contains a scattering of reports concerning reaction kinetics in aqueous media containing ionic or nonionic surfactants. However, substantial insight into this area was first achieved in 1959 by Duynstee and Grunwald in their study of the effects of cationic and anionic surfactants on the rate of alkaline fading of cationic triphenylmethane dyes.[125] Since that time, related studies have been appearing at an increasing rate, and interest is still growing.

Association colloids have interfacial regions containing ionic and polar head groups and ionic and polar solutes may be incorporated in this region.

Apolar cores of micelles, which exclude polar and ionic solutes and interfacial regions, are accessible to these solutes and to water. Consideration of the dimensions of head groups and apolar tails indicates that the volume of the interfacial region is approximately half that of the total micelle. Solutions of dilute surfactants are isotropic, but there is extensive physical evidence that they are dispersions of submicroscopic particles which form a micellar pseudophase distinct from the aqueous pseudophase. The interfacial region is highly anisotropic and in ionic micelles there is considerable neutralization of head groups by counterions. The intrinsic heterogeneous character of a micellar solution requires the developments of novel concepts in reaction kinetics since deviations from conventional rate laws applicable to homogeneous systems are frequently observed.[126–128] In particular, the fact has to be taken into account that compartmentation of the reactants occurs as a consequence of their association with the surfactant aggregates.[127]

In a homogeneous surfactant solution (above critical micelle concentration) the reactive site of substrate may exist in one or more of the following environments: the micelle interior, the micelle water interface, and the bulk solvent. One of the most important processes leading to the micellar effects on reactions is the solubilization of substrates in micellar interiors. It is possible to solubilize water insoluble substances or to increase the solubilities of slightly soluble ones in aqueous micellar solutions. They penetrate toward the hydrocarbon-like cores of the micelles.[129–137] Since the solvent molecules penetrate beyond the polar head groups, solute in the solvent phase can interact

both with the nonpolar chains of surfactant molecules and with polar head groups. Thus the micellar phase may be referred to as amphipathic, having affinity for both polar and nonpolar species. Micellar cores behave like an organic phase and the hydrophobic forces play an important role in the solubilization process.[138]

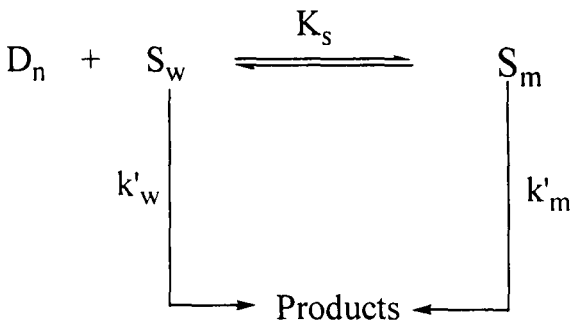
The pathways and rates of reactions in micelles are affected by how deeply the solubilized species is located within the micelle. Both electrostatic and hydrophobic forces play a role in determining the binding site of a solute inside the micelle, and both the structure of the amphiphile and the solute are of great importance in determining the extent of solublization and the penetration of solute into the micelles.[111]

Another fundamental process in micellar catalysis or inhibition is the counterion binding to micelles. Micelles can either attract the reactive ions or repel them depending upon the electrical charge of their head groups. Thus, micelles may bring the solubilized substrates and reactive ions together or keep them apart such that the reactions are speeded up or inhibited. Another way by which micelles can catalyze a reaction is the stabilization of intermediates as bound counterions.[139,140] Sometimes, even substrates are bound to micelles as their counterions.[141]

Most kinetic treatments are based on so-called pseudophase model. This model has been generally accepted on the reasonable assumption that for most activated thermal chemical reactions, transfer of material between water and

micelle is so fast that reaction does not perturb the equilibrium distribution of reactants between the pseudophases. This generalization cannot be applied to photochemical reactions, where some steps of the reaction may be very rapid and therefore faster than solute transfer.[94,142] Provided that equilibrium is maintained between the aqueous and the micellar pseudophases, the overall reaction rate will be the sum of rates in water and in the micelles and will therefore depend on the distribution of reactants between each pseudophase and the appropriate rate constants in the two pseudophases.

Menger and Portnoy[100] developed a quantitative treatment that adequately described inhibition of ester saponification by anionic micelles. Micelles bound hydrophobic esters, and anionic micelles excluded hydroxide ions and so inhibited the reaction, whereas cationic micelles speeded saponification by attracting hydroxide ions.[143] Provided that only substrate distribution has to be considered, which is the situation for micelle-inhibited bimolecular or spontaneous unimolecular reactions, Scheme 1.3 shows the substrate distribution and reaction in each pseudophase.[144]



Scheme 1.3

In the Scheme 1.3, D_n denotes micellized surfactant, S is substrate, subscripts w and m denote aqueous and micellar pseudophases, respectively, and k'_w and k'_m are first-order rate constants. The binding constant, K_s, is written in terms of the molarity of micellized surfactant, but it could equally be written in terms of the molarity of micelles. The concentration of micellized surfactant is that of total surfactant less that of monomer, which is assumed to be given by the cmc.

The experimental rate constant k_Ψ for Scheme 1.3 is a weighted sum of the two constants k'_w and k'_m

$$k_\Psi = f_w k'_w + f_m k'_m = f_w k'_w + (1 - f_w) k'_m \qquad (1.6)$$

where f_w and f_m are the fractions of substrate in the bulk solution and solubilized in the micelles, respectively. The second version of Eq. (1.6) arises from the recognition that $f_w + f_m = 1$. The equilibrium constant, K_s, in Scheme 1.3 can be written as

$$K_s = \frac{[S_m]}{[S_w][D_n]} = \frac{f_m [S_t]}{[D_n] f_w [S_t]} = \frac{f_m}{[D_n](1-f_m)} \qquad (1.7)$$

where $[S_t]$ is the total substrate concentration.

From Eq. (1.7)

$$f_w = (1 + K_s[D_n])^{-1} \qquad (1.8)$$

which, on substitution in Eq. (1.6), gives

$$k_{\psi} = \frac{k'_w + k'_m K_s[D_n]}{1 + K_s[D_n]} \qquad (1.9)$$

This equation is similar in form to the Michaelis–Menten equation of enzyme kinetics, although the analogy is limited because most enzymatic reactions are studied with substrate in large excess over enzyme. Equation (1.9) could be rearranged to give Eq. (1.10), which is formally similar to the *Lineweaver–Burk equation and which permits calculation of* k'_m *and* K_s *provided* that k'_w is known.[100,143]

$$\frac{1}{(k'_w - k_{\psi})} = \frac{1}{(k'_w - k'_m)} + \frac{1}{(k'_w - k'_m)K_s[D_n]} \qquad (1.10)$$

Equations (1.9) and (1.10) have been applied successfully to micellar catalyzed unimolecular reactions and to many micellar mediated reactions. The observations suggest that the pseudophase model is useful in analyzing micellar catalysis and inhibition. These equations, however, depend on some major assumptions, in particular that the cmc gives the concentration of monomeric surfactant and the rate and binding constants in the micellar pseudophase are unaffected by reactants and products.

E. Statement of the Problem

Cerium(IV) as an oxidant has been employed both in mechanistic[16,29,49,145–159] as well as synthetic[160–162] studies despite the fact the speciation of sulfato–cerium(IV) species is still not established

conclusively[163–165] in sulfuric acid medium. Cerium(III) is the only reduction product of cerium(IV) as the latter is one of a group of metal ion oxidants which apparently react only via one–electron steps. Cerium(III) has been found useful for the plants as well as animals.[15]

Due to very important role of cerium(IV) (as an oxidant), the oxidation of carbohydrates by cerium(IV) has received attention for a long time,[9,35–53] but the same in presence of surfactants has not been studied so far.

Effect of organized structures (*e.g.*, micelles being one of them) on the rate of electron transfer reactions has been receiving considerable attention too.[166–168] A number of interfacial electron transfer processes have been investigated in polyelectrolytes, vesicles and micellar surfaces including photoredox reactions.[94] The interest in this subject arises from the similarity with the biological processes. Therefore, the present work was undertaken to study the effect of surfactant micelles on the kinetics and mechanism of oxidation of carbohydrates by cerium(IV). For this purpose two aldopentoses (D(+)xylose and L(+)arabinose), two aldohexoses (D(+)glucose and D(+)mannose), and two ketohexoses (D(–)fructose and L(–)sorbose) were used. The surfactants used in the study were cationic cetyltrimethylammonium bromide (CTAB) and anionic sodium dodecyl sulfate (SDS).

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CHAPTER 2

EXPERIMENTAL

A. Materials

Table 2.1 summarizes the chemicals which were used throughout the study. The surfactants, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS), as well as all other chemicals were used as such without further purification.

B. Preparation of Solutions

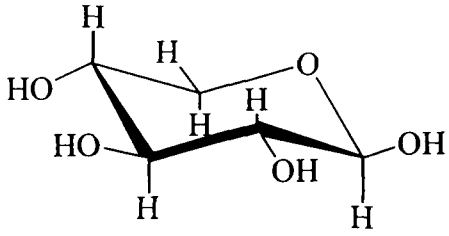
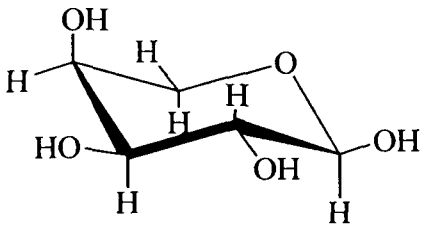
The solutions were prepared by directly dissolving the weighed samples in doubly-distilled water (distillation carried out over alkaline $KMnO_4$ in an all-Pyrex distillation set-up) having specific conductivity 1–2 x 10^{-6} S cm^{-1}. The compound ammonium ceric nitrate is available as a primary standard,[1] and standard solutions were made by direct weighing followed by dilution in a volumetric flask. Fresh solutions of carbohydrates were prepared before use.

C. Kinetic Measurements

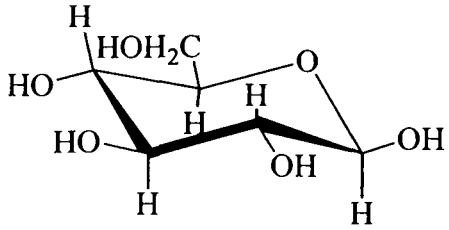
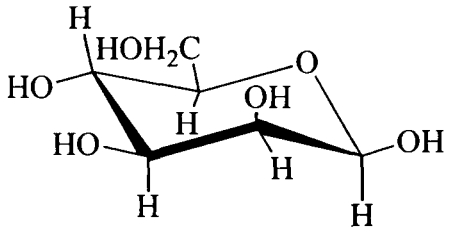
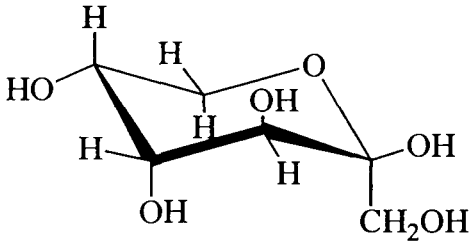
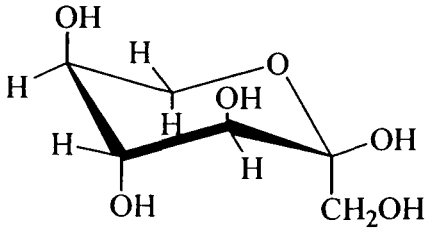
The kinetic experiments were carried out at constant temperatures controlled within ±0.1 °C in a thermostat which was designed and assembled in the laboratory with commercially available components. Known volumes of all the reactants (except reductant, *i.e.*, monosaccharide) were taken in a three-necked reaction vessel equipped with a double-surface water condenser to prevent evaporation. The aqueous solution of reductant was taken in another flask. Both containers were then placed in the thermostat at the desired

TABLE 2.1:

Names and structural formulae of the chemicals used.

Name	Abbreviation	Structure/Formula	Make	% Purity
Surfactants				
Cetyltrimethylammonium bromide	CTAB	$CH_3(CH_2)_{15}N^+(CH_3)_3\ Br^-$	BDH (England)	>99
Sodium dodecyl sulfate	SDS	$CH_3(CH_2)_{11}OSO_3^-\ Na^+$	Sigma (USA)	99
Oxidant				
Ammonium ceric nitrate		$(NH_4)_2\ [Ce(NO_3)_6]$	Qualigens (India)	99
Reductants				
D(+)Xylose			s.d. fine (India)	99
L(+)Arabinose			Sigma (USA)	99

Contd...

D(+)Glucose		Merck (India)	99
D(+)Mannose		s.d. fine (India)	99
D(–)Fructose		Merck (India)	99
L(–)Sorbose		Fluka (Switzerland)	98

Contd...

Acid			
Sulfuric acid	H_2SO_4	Merck (India)	98
Salts			
Sodium sulfate	Na_2SO_4	Merck (India)	≥98
Sodium hydrogen sulfate monohydrate	$NaHSO_4.H_2O$	s.d. fine (India)	99
Sodium bromide	NaBr	s.d. fine (India)	99
Sodium chloride	NaCl	Merck (India)	99.9
Sodium nitrate	$NaNO_3$	Merck (India)	99
Other			
Acrylonitrile	C_3H_3N	s.d. fine (India)	99

temperature for sufficient time to attain thermal equilibrium. Required volume of the reductant was then added to other reactants (cerium(IV), H_2SO_4, *etc.*) and zero time noted when half of the monosaccharide solution had been added. Monosaccharide was always in excess (*ca.* ten times) of cerium(IV) solution in order to maintain pseudo-first-order conditions. The progress of the reaction was followed at 385 nm by monitoring the absorbance changes of cerium(IV) (cerium(III) is transparent at this wavelength)[2,3] with a Bausch and Lomb Spectronic-20 spectrophotometer. For this purpose, aliquots of the reaction mixture were taken out at definite time intervals and cooled in an ice bath to quench the reaction before each measurement. The pseudo-first-order rate constants in absence (k_{obs}, s^{-1}) and presence of surfactants (k_ψ, s^{-1}) were calculated from the linear parts of the plots of log(absorbance) *versus* time by carrying out reactions up to ~80% completion.

The dependence of k_{obs} or k_ψ was obtained as a function of [oxidant], [H_2SO_4], [reductant], [SO_4^{2-}], [HSO_4^-], [surfactant], temperature and [salt]. The results are given in Chapter 3.

D. Determination of cmc

(a) by conductivity measurements

Aqueous solutions of surfactants show normal electrical conductivities and follow the Onsager equation at very low concentrations. Deviations from Onsager plots occur after critical concentrations of the surfactants. Above the

critical concentration a sharp fall in conductance is generally observed. This is interpreted as caused by micelle formation owing to the presence of highly charged ions above the critical concentration.[4]

It is well known[5] that the specific conductivity is linearly related to the surfactant concentration in both the pre-micellar as well as in the post-micellar regions, the slope in the pre-micellar region being greater than that in the post-micellar region. The intersection point between the two straight lines gives the cmc.

The conductivity measurements were made using an ELICO (Hyderabad, India) bridge (type CM 82T) with platinized electrodes (cell constant = 1.02 cm^{-1}). The conductivity of the solvent (taken in a glass container which was kept in a thermostat at the desired temperature) was measured before the addition of CTAB. Small amounts of CTAB were added successively, mixed well and the conductivity was recorded. The specific conductivity was calculated applying solvent corrections. The cmc values obtained under different conditions are listed in Table 2.2.

(b) by surface tension measurements

Due to high concentration of H_2SO_4 (1.83 mol dm^{-3}) in our experimental conditions, it was not possible to measure the cmc of CTAB conductimetrically in presence of the acid. Therefore, the surface tension measurements were also performed for obtaining the cmc in presence of H_2SO_4.

TABLE 2.2:

Critical micelle concentration (cmc) values of CTAB in different solutions at 40 °C (by conductimetric method).[a]

Solution	10^4 cmc (mol dm^{-3})
Water	10.2 (9.8, 11.5)[b]
Water + cerium(IV)	10.0
Water + D(+)xylose	10.0
Water + L(+)arabinose	10.0
Water + D(+)glucose	10.0
Water + D(+)mannose	9.9
Water + D(–)fructose	9.9
Water + L(–)sorbose	9.5
Water + cerium(IV) + D(+)xylose	8.3
Water + cerium(IV) + L(+)arabinose	8.8
Water + cerium(IV) + D(+)glucose	10.0
Water + cerium(IV) + D(+)mannose	9.8
Water + cerium(IV) + D(–)fructose	9.9
Water + cerium(IV) + L(–)sorbose	9.4

[a]$[Ce(IV)]_T = 1.0 \times 10^{-5}$ mol dm^{-3}, $[carbohydrate]_T = 4.0 \times 10^{-2}$ mol dm^{-3}.

[b]The literature values at different temperatures (35 and 45 °C) by conductance measurement are quoted in the parenthesis.[6]

Surface tension is probably the most common means of determining the cmc. Below the cmc, surfactant molecules position themselves at the air\water interface and thus lower the surface tension. Above the cmc, any added surfactant monomer prefers to join micelle rather than to enter the interfacial film. Consequently, a plot of surface tension *versus* concentration decreases steeply below the cmc and levels off above it, the break in the plot is taken as the cmc. The method is fast, convenient, and non-destructive to the surfactant.

The surface tension was measured by the ring detachment method using a S.D. Hardson tensiometer (Kolkata, India). The addition of surfactant solution to the solvent was similar as described under conductivity measurements. The cmc values of CTAB obtained under different experimental conditions are given in Table 2.3.

We see remarkable changes in the aggregation behavior of CTAB in presence of H_2SO_4. These results of cmc decrease are in accord with the earlier observations of micelle formation at relatively low surfactant concentration with the rise of water content.[7–10]

E. Product Analysis

(a) characterization of cerium(III)

To identify the reaction product of cerium(IV) present in the reaction mixture, several kinetic experiments were performed taking $[Ce(IV)]_T = 1.0 \times 10^{-3}$ mol dm^{-3}, $[reductant]_T = 4.0 \times 10^{-2}$ mol dm^{-3} and $[H_2SO_4] = 1.83$ mol dm^{-3}

TABLE 2.3:

Critical micelle concentration (cmc) values of CTAB in different solutions at 40 °C (by surface tension measurements).[a]

Solution	10^4 cmc (mol dm^{-3})
Water	9.9 (8.0)[b]
Water + cerium(IV)	2.0
Water + H_2SO_4	0.21
Water + D(+)xylose	8.3
Water + L(+)arabinase	9.1
Water + D(+)glucose	9.9
Water + D(+)mannose	8.3
Water + D(−)fructose	9.1
Water + L(−)sorbose	9.1
Water + cerium(IV)+ H_2SO_4 + D(+)xylose	0.20
Water + cerium(IV)+ H_2SO_4 + L(+)arabinose	0.15
Water + cerium(IV)+ H_2SO_4 + D(+)glucose	0.16
Water + cerium(IV)+ H_2SO_4 + D(+)mannose	0.13
Water + cerium(IV)+ H_2SO_4 + D(−)fructose	0.16
Water + cerium(IV)+ H_2SO_4 + L(−)sorbose	0.15

[a]$[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[carbohydrate]_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}.

[b]The literature value at 25 °C by surface tension measurement.[6]

at 40 °C. The spectra of the mixtures were recorded at different time intervals, which show that, as the reactions progress, the peak at 385 nm (which was observed at zero reaction time) decreases. At the end of the reactions, under the above experimental kinetic conditions, the cerium(IV) peak was found absent but appearance of any new peak was not observed as well (for example, see Fig. 2.1, A, for Ce(IV)–fructose reaction). These spectral studies show that the reaction product formed in the reaction of cerium(IV) and carbohydrates is transparent. This is the indication of the presence of cerium(III)[2,3] as one of the reaction products.

Same behavior of the spectra was observed in presence of CTAB (Fig. 2.1, B) indicating that cerium(III) is formed in CTAB medium also.

(b) lactones and aldonic acids

Qualitative analyses of the oxidized reaction mixtures with the excess [reductant] over [Ce(IV)] (the kinetic condition) in presence of H_2SO_4 were performed for each carbohydrate. After the kinetic experiment was over, a part of the oxidized reaction mixture was treated with alkaline hydroxylamine solution, and the presence of lactone in the reaction mixture was tested by $FeCl_3$ — HCl blue test.[11,12]

To the other part of the reaction mixture, barium carbonate was added to make the solution neutral.[13] $FeCl_3$ solution that had been colored violet with phenol when added to this reaction mixture gave a bright-yellow coloration,[14] indicating the presence of aldonic acid.

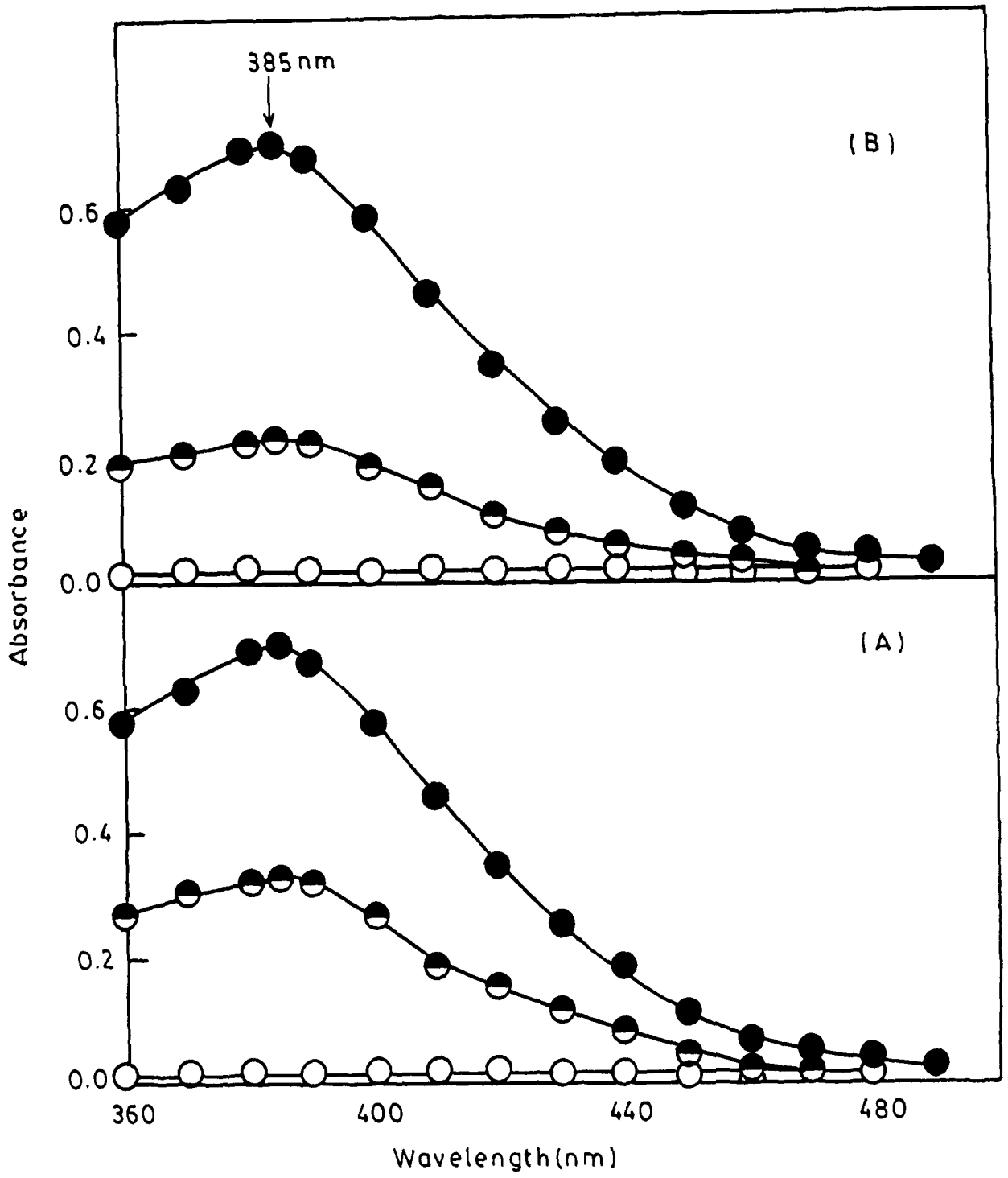


Fig. 2.1: Absorption spectra of the reaction product of cerium(IV) and D(–)fructose in absence (A) and presence (B) of CTAB at 40 °C: (●) immediately after mixing the reactants, $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[D(-)fructose]_T$ = 4.0 x 10^{-2} mol dm^{-3} and $[H_2SO_4]_T$ = 1.83 mol dm^{-3}; (◓) after 30 min and (○) after 120 min.

(c) free radical detection

Acrylonitrile monomer was used to test the presence of free radicals in the reaction mixtures. Appearance of a precipitate of white polymeric product was observed when monomer solution (30%) was added to reaction mixtures containing $[Ce(IV)]_T = 1.0 \times 10^{-3}$ mol dm^{-3}, $[reductant]_T = 4.0 \times 10^{-2}$ mol dm^{-3} and $[H_2SO_4]_T = 1.83$ mol dm^{-3}. This confirms the formation of free radicals during the oxidation of carbohydrates by cerium(IV).

(d) stoichiometry

To determine the oxidant : reductant stoichiometric ratios, a series of kinetic runs with a fixed concentration of cerium(IV) (= 1.0×10^{-3} mol dm^{-3}) in excess and different concentrations of reductant in presence of 1.83 mol dm^{-3} H_2SO_4 were performed. After completion of the reactions, the unconsumed oxidant was estimated spectrophotometrically. The consumption ratios, *i.e.*, the number of moles of cerium(IV) consumed per mole of carbohydrate (calculated by assuming that the carbohydrates were totally consumed under these conditions) were found to be (cerium(IV) : carbohydrate) 6 : 1, 4 : 1, 4 : 1, 4 : 1, 5 : 1, 3 : 1, for D(+)xylose, L(+)arabinose, D(+)glucose, D(+)mannose, D(–)fructose and L(–)sorbose, respectively. Due to autoaccelaration nature of the reaction (*vide infra*), the exact stoichiometry equation and products formed are difficult to predict. However, the carbohydrates have been used in sufficient excess throughout the kinetic investigations to ensure that the rate of reduction of the cerium(IV) is proportional to the rate of oxidation of organic substrates

themselves, but not to the rate of destruction of any reactive organic intermediates.[15] Moreover, since the initial rate of consumption of cerium(IV) under these conditions was always first-order, the rate of oxidation of the intermediate products cannot be kinetically significant.[15]

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CHAPTER 3

RESULTS AND DISCUSSION

A. Results

In aqueous H_2SO_4 media, cerium(IV) is both thermodynamically and kinetically weaker as an oxidizing agent. However, due to greater stability[1,2] and not requiring any special precaution to prevent its photochemical decomposition[3] (which occurs spontaneously in aqueous $HClO_4$), cerium(IV) in aqueous H_2SO_4 media is very often used as an oxidant. The present work, therefore, deals with the redox reactions of cerium(IV) and carbohydrates carried out in H_2SO_4 media in the absence and presence of surfactants.

The method of kinetic measurements has already been described in Chapter 2. The kinetics was investigated at several initial [Ce(IV)], [carbohydrate], $[H_2SO_4]$, $[SO_4^{2-}]$, $[HSO_4^-]$, [surfactant], temperature, and [salt]. Figs. 3.1–3.6 show examples of some of the kinetic curves from which the rate constants for the oxidations were obtained. As can be seen, the plots of log(absorbance) *versus* time deviate from linearity: this suggests the involvement of two reaction paths, *i.e.*, the initial slow stage followed by a relatively faster step.[4,5] The time at which deviations commenced was found to decrease with increase in [carbohydrate] and temperature whereas increasing the acid concentration increased it. A choice was, therefore, made to study the detailed kinetics at $[H_2SO_4] = 1.83$ mol dm^{-3} (except when the effect of $[H_2SO_4]$ was seen).

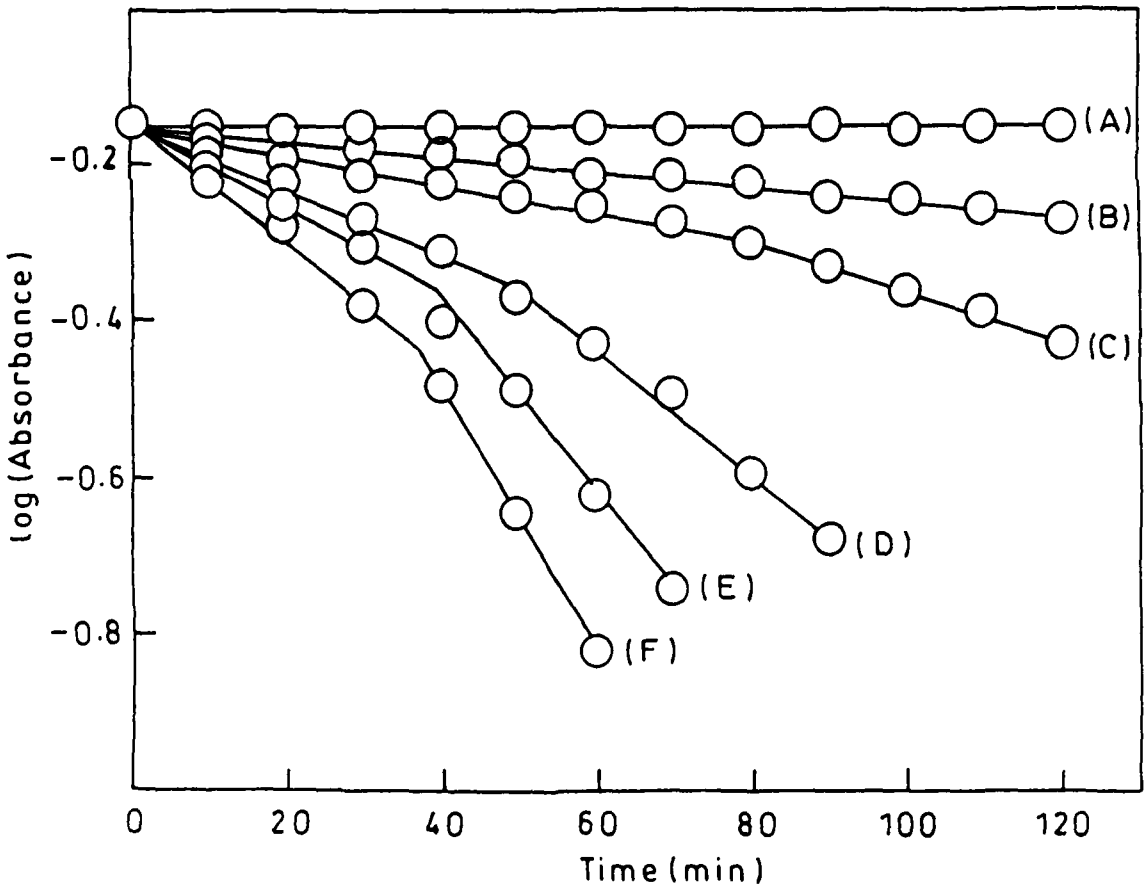


Fig. 3.1: Plots of log(absorbance) *versus* time showing the noncatalytic and autocatalytic paths for the oxidation of D(+)xylose by cerium(IV) (= 1.0 x 10^{-3} mol dm^{-3}) in presence of H_2SO_4 (= 1.83 mol dm^{-3}) at 40 °C. *Conditions:* $[D(+)xylose]_T$ = 0.0 (A), 1.0 (B), 2.0 (C), 4.0 (D), 6.0 (E) and 8.0 x 10^{-2} mol dm^{-3} (F); [CTAB] = 50.0 x 10^{-4} mol dm^{-3} (A).

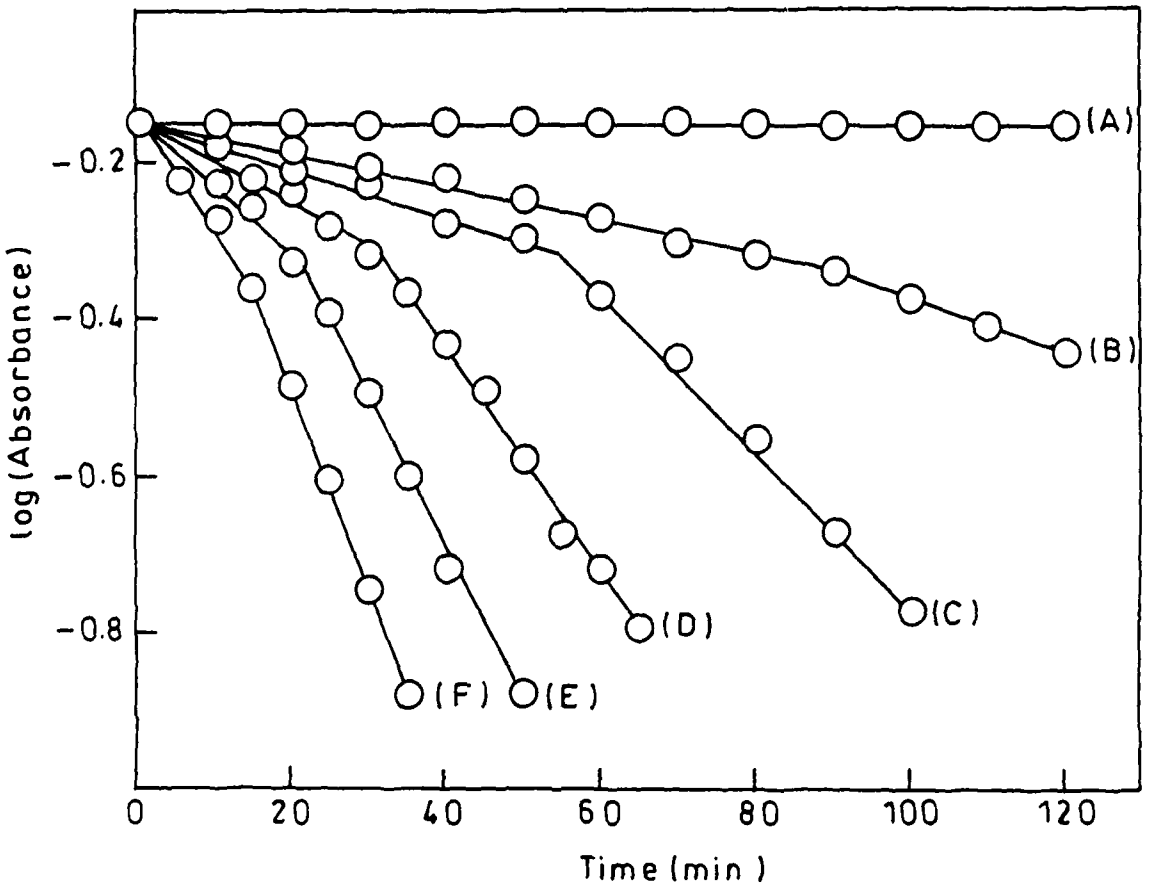


Fig. 3.2: Plots of log(absorbance) *versus* time showing the noncatalytic and autocatalytic paths for the oxidation of L(+)arabinose by cerium(IV) (= 1.0×10^{-3} mol dm^{-3}) in presence of H_2SO_4 (= 1.83 mol dm^{-3}) at 40 °C. *Conditions:* $[L(+)arabinose]_T$ = 0.0 (A), 1.0 (B), 2.0 (C), 4.0 (D), 6.0 (E) and 8.0×10^{-2} mol dm^{-3} (F); [CTAB] = 50.0×10^{-4} mol dm^{-3} (A).

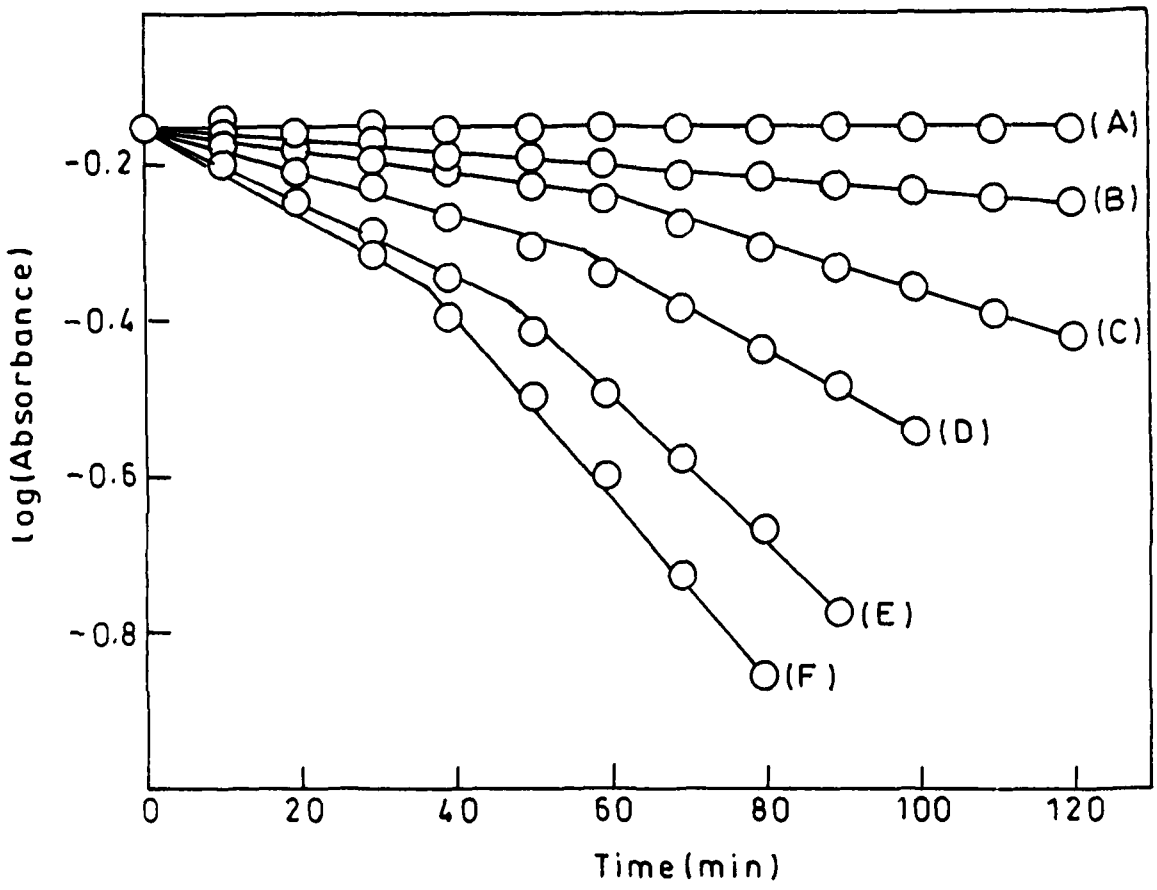


Fig. 3.3: Plots of log(absorbance) *versus* time showing the noncatalytic and autocatalytic paths for the oxidation of D(+)glucose by cerium(IV) (= 1.0 x 10^{-3} mol dm^{-3}) in presence of H_2SO_4 (= 1.83 mol dm^{-3}) at 40 °C. *Conditions:* $[D(+)glucose]_T$ = 0.0 (A), 1.0 (B), 2.0 (C), 4.0 (D), 6.0 (E) and 8.0 x 10^{-2} mol dm^{-3} (F); [CTAB] = 50.0 x 10^{-4} mol dm^{-3} (A).

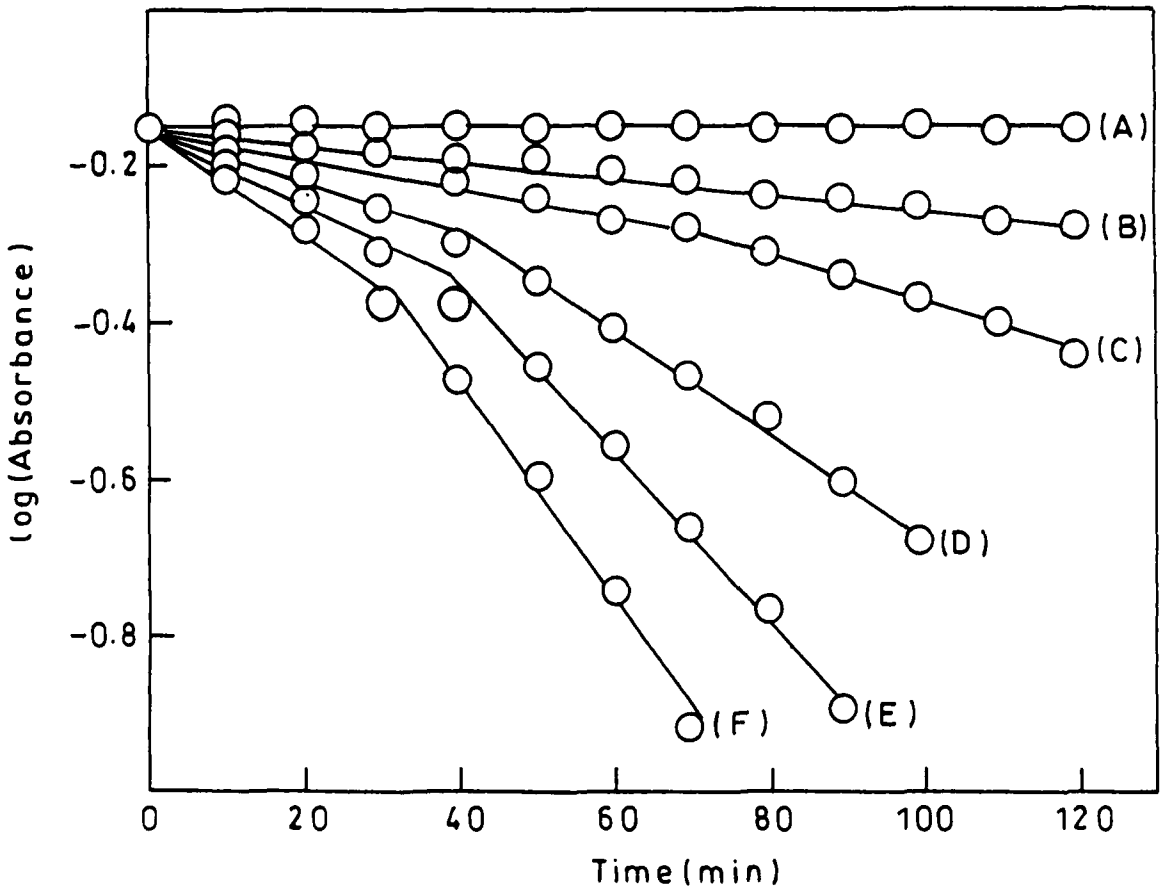


Fig. 3.4: Plots of log(absorbance) *versus* time showing the noncatalytic and autocatalytic paths for the oxidation of D(+)mannose by cerium(IV) (= 1.0 x 10^{-3} mol dm^{-3}) in presence of H_2SO_4 (= 1.83 mol dm^{-3}) at 40 °C. *Conditions:* $[D(+)mannose]_T$ = 0.0 (A), 1.0 (B), 2.0 (C), 4.0 (D), 6.0 (E) and 8.0 x 10^{-2} mol dm^{-3} (F); [CTAB] = 50.0 x 10^{-4} mol dm^{-3} (A).

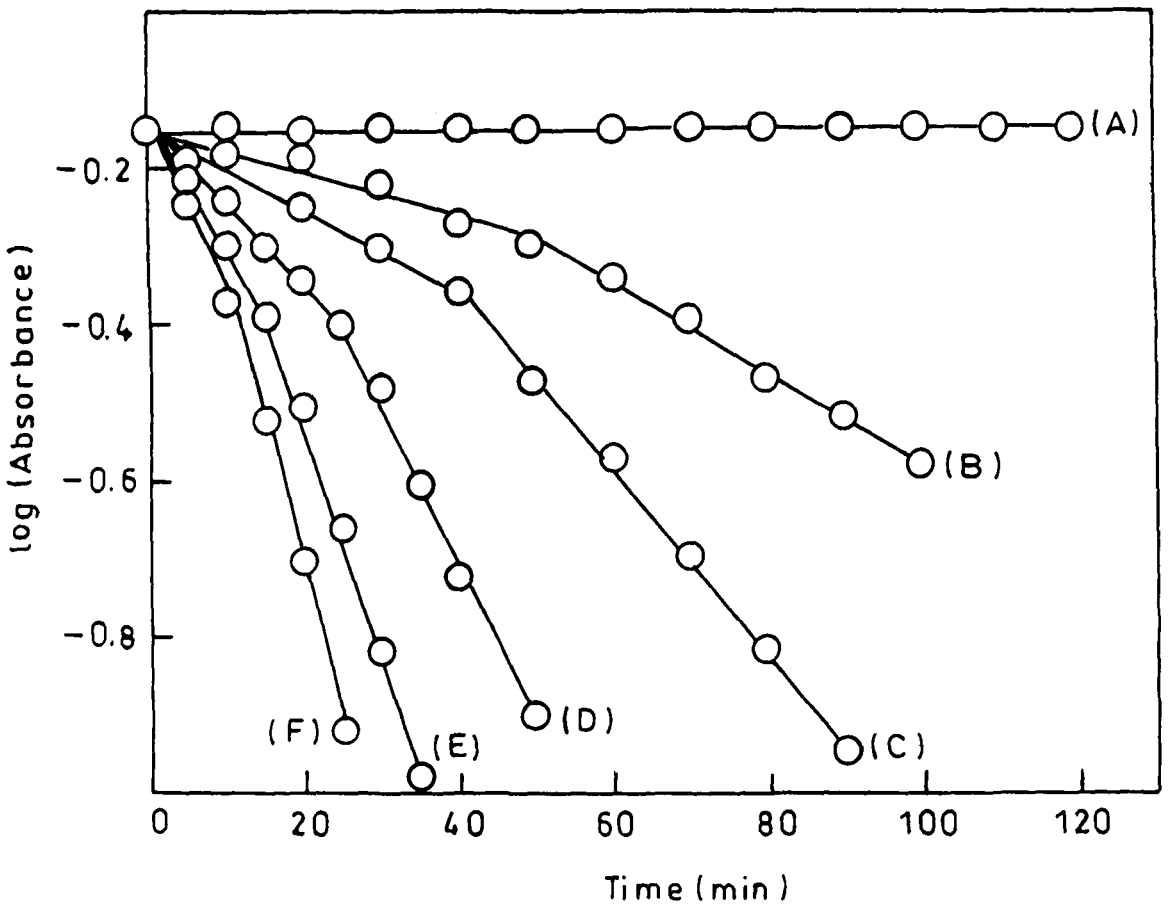


Fig. 3.5: Plots of log(absorbance) *versus* time showing the noncatalytic and autocatalytic paths for the oxidation of D(–)fructose by cerium(IV) (= 1.0 x 10^{-3} mol dm^{-3}) in presence of H_2SO_4 (= 1.83 mol dm^{-3}) at 40 °C. *Conditions:* $[D(-)fructose]_T$ = 0.0 (A), 1.0 (B), 2.0 (C), 4.0 (D), 6.0 (E) and 8.0 x 10^{-2} mol dm^{-3} (F); [CTAB] = 50.0 x 10^{-4} mol dm^{-3} (A).

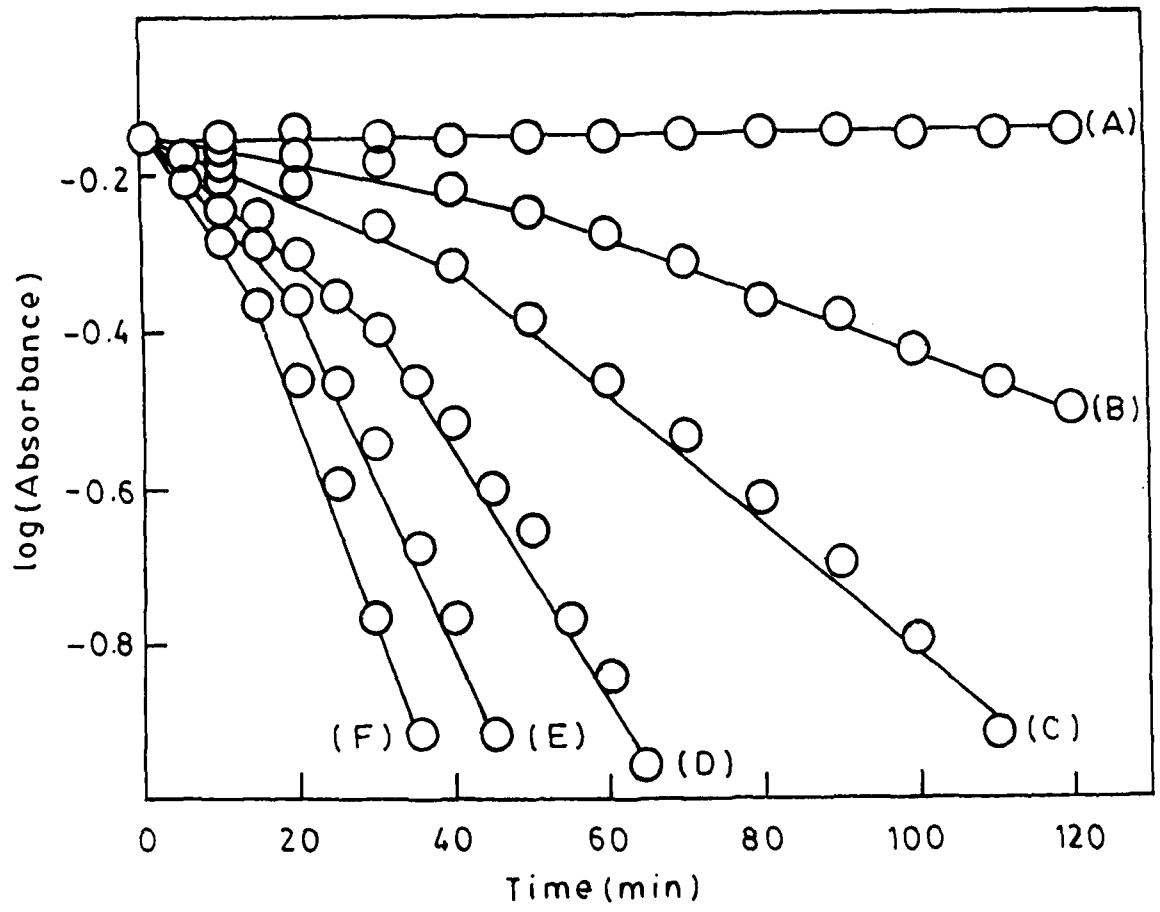


Fig. 3.6: Plots of log(absorbance) *versus* time showing the noncatalytic and autocatalytic paths for the oxidation of L(–)sorbose by cerium(IV) (= 1.0×10^{-3} mol dm^{-3}) in presence of H_2SO_4 (= 1.83 mol dm^{-3}) at 40 °C. *Conditions:* $[L(-)sorbose]_T$ = 0.0 (A), 1.0 (B), 2.0 (C), 4.0 (D), 6.0 (E) and 8.0×10^{-2} mol dm^{-3} (F); [CTAB] = 50.0×10^{-4} mol dm^{-3} (A).

The values of pseudo-first-order rate constants were evaluated from the slopes of the initial parts (first stage) of the linear plots. An interesting feature of this reaction is the autocatalysis, due to the catalytic role of one of the oxidation products.

Effect of [oxidant] on the rate

The effect of concentration of oxidant on the rate constants was determined by carrying out kinetic runs at different [Ce(IV)]. The reductant concentrations were kept constant with 1.83 mol dm^{-3} H_2SO_4 at 40 °C. The pseudo-first-order rate constants (k_{obs}) obtained at different cerium(IV) concentrations are given in Tables 3.1–3.6. The results show that the values of rate constants are independent of the initial oxidant concentration. Thus, it is concluded that the order of the reaction with respect to [Ce(IV)] is one. The rate law would then be

$$\text{rate} = -d[Ce(IV)]/dt = k_{obs}[Ce(IV)]_T \qquad (3.1)$$

Effect of [reductant] on the rate

The effect of the concentrations of the reductants were studied keeping all other experimental conditions constant. The results are given in Tables 3.7–3.12.

The plots of rate constant *versus* [reductant] (Figs. 3.7–3.12) were found to be linear and passing through the origin indicating first-order dependence on [reductant].

TABLE 3.1:

Effect of $[Ce(IV)]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(+)xylose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[D(+)xylose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}

$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}

Temperature $= 40$ °C

$10^3[Ce(IV)]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
0.6	1.9	3.0
0.8	1.9	2.9
0.9	1.8	2.8
1.0	1.7	2.5
1.1	1.4	2.6
1.2	1.3	2.5
1.3	1.3	2.3

[a]$[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.2:

Effect of $[Ce(IV)]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of L(+)arabinose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[L(+)arabinose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}

$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}

Temperature $= 40$ °C

$10^3[Ce(IV)]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
0.6	2.5	3.7
0.8	2.2	3.5
0.9	2.3	3.7
1.0	2.2	3.6
1.1	2.2	3.6
1.2	2.2	3.7
1.3	2.1	3.6

[a]$[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.3:

Effect of $[Ce(IV)]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(+)glucose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[D(+)glucose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}
$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}
Temperature $= 40$ °C

$10^3[Ce(IV)]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
0.6	1.3	2.6
0.8	1.1	2.4
0.9	1.1	1.8
1.0	1.1	1.7
1.1	1.0	1.7
1.2	0.8	1.1
1.3	0.8	1.6

[a]$[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.4:

Effect of $[Ce(IV)]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(+)mannose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[D(+)mannose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}
$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}
Temperature $= 40$ °C

$10^3[Ce(IV)]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
0.6	1.6	2.7
0.8	1.6	2.6
0.9	1.5	2.4
1.0	1.5	2.4
1.1	1.5	2.3
1.2	1.6	4.2
1.3	1.5	2.4

[a]$[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.5:

Effect of $[Ce(IV)]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(–)fructose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[D(-)fructose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}
$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}
Temperature $= 40$ °C

$10^3[Ce(IV)]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
0.6	4.8	5.4
0.8	4.5	5.2
0.9	4.2	5.2
1.0	3.8	5.2
1.1	4.2	5.2
1.2	3.6	5.2
1.3	4.0	5.2

[a]$[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.6:

Effect of $[Ce(IV)]_T$ on the pseudo-first-order rate constants (k_{obs} or k_Ψ) for the oxidation of L(–)sorbose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[L(-)sorbose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}

$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}

Temperature $= 40$ °C

$10^3[Ce(IV)]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\Psi$ (s^{-1})	
	Aqueous	CTAB[a]
0.6	3.2	5.0
0.8	3.3	4.9
0.9	3.1	4.9
1.0	3.2	4.7
1.1	3.0	4.4
1.2	2.7	4.2
1.3	2.4	4.1

[a]$[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.7:

Effect of $[D(+)xylose]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(+)xylose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}

$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature = 40 °C

$10^2[D(+)xylose]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
1.0	0.4	0.7
2.0	0.7	1.3
3.0	1.2	2.2
4.0	1.7	2.5
5.0	1.9	3.0
6.0	2.4	3.7
7.0	2.8	4.3
8.0	3.2	5.4
9.0	3.5	5.8

[a] $[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.8:

Effect of $[L(+)arabinose]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of L(+)arabinose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}

$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature = 40 °C

$10^2[L(+)arabinose]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
1.0	0.8	1.0
2.0	1.2	1.5
3.0	1.5	2.8
4.0	2.2	3.6
5.0	2.6	4.2
6.0	3.5	5.2
7.0	4.2	6.1
8.0	5.4	6.5
9.0	5.9	7.5

[a] $[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}

TABLE 3.9:

Effect of $[D(+)glucose]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(+)glucose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ $= 1.0 \times 10^{-3}$ mol dm^{-3}

$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}

Temperature $= 40$ °C

$10^2[D(+)glucose]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
1.0	0.3	0.4
2.0	0.4	1.0
3.0	0.8	1.2
4.0	1.1	1.7
5.0	1.3	1.8
6.0	1.8	2.3
7.0	1.9	2.6
8.0	2.3	3.0
9.0	2.5	3.3

[a]$[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.10:

Effect of $[D(+)mannose]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(+)mannose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ $= 1.0 \times 10^{-3}$ mol dm^{-3}

$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}

Temperature $= 40$ °C

$10^2[D(+)mannose]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
1.0	0.4	0.6
2.0	0.7	1.0
3.0	1.4	1.6
4.0	1.5	2.4
5.0	1.7	3.1
6.0	2.3	3.5
7.0	2.5	3.7
8.0	3.1	4.3
9.0	3.3	5.0

[a] $[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.11:

Effect of $[D(-)fructose]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(–)fructose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ $= 1.0 \times 10^{-3}$ mol dm^{-3}

$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}

Temperature $= 40$ °C

$10^2[D(-)fructose]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
1.0	1.0	1.2
2.0	1.9	2.4
3.0	2.6	3.7
4.0	3.8	5.2
5.0	5.1	6.1
6.0	6.1	7.8
7.0	6.6	9.0
8.0	8.9	10.5
9.0	10.0	11.9

[a] $[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.12:

Effect of $[L(-)sorbose]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of L(–)sorbose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}

$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature = 40 °C

$10^2[L(-)sorbose]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
1.0	0.8	1.4
2.0	1.6	2.7
3.0	2.5	4.0
4.0	3.2	4.7
5.0	3.8	6.0
6.0	4.2	7.1
7.0	5.2	8.2
8.0	5.6	9.5
9.0	6.9	11.1

[a]$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}

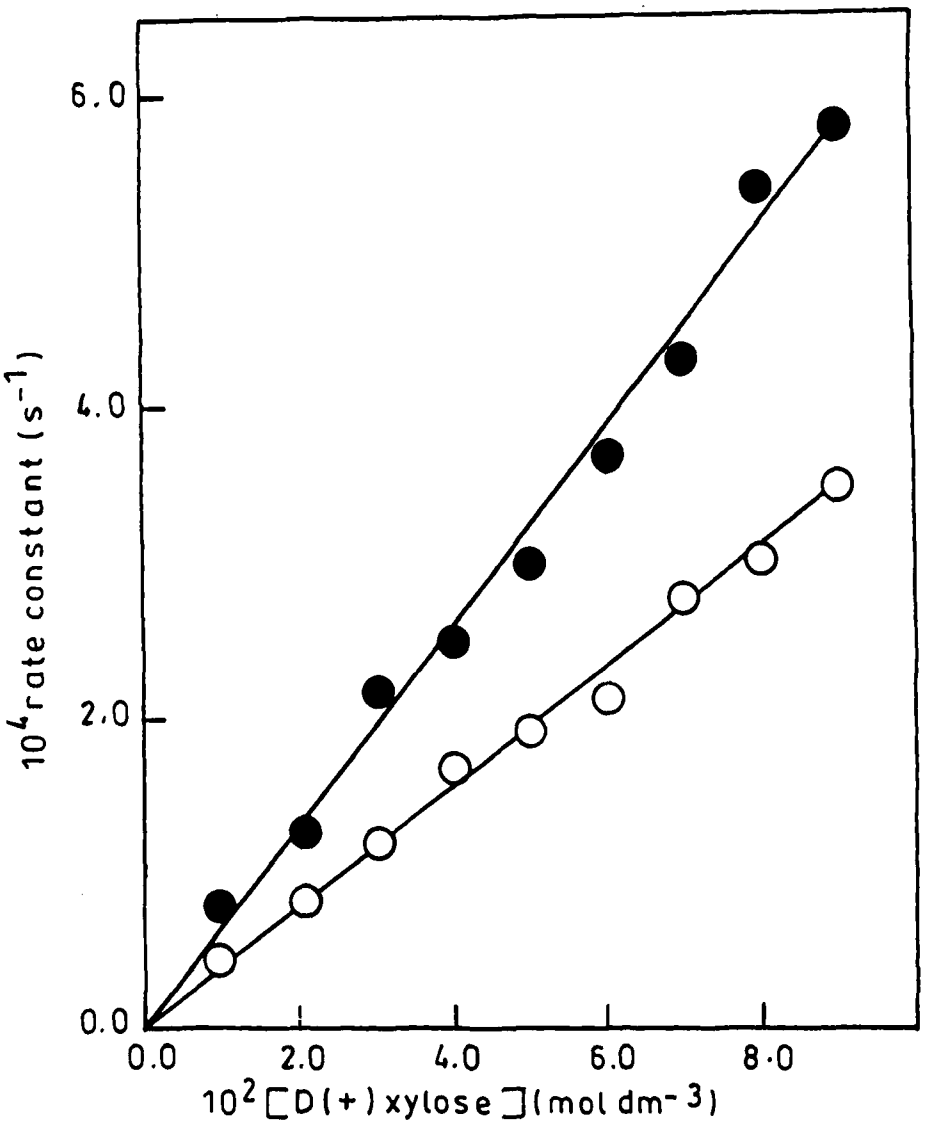


Fig. 3.7: Plots of rate constants *versus* $[D(+)xylose]_T$ for the oxidation of D(+)xylose by cerium(IV). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, $[CTAB]_T$ = 0.0 (○), 50.0 x 10^{-4} mol dm^{-3} (●), temperature = 40 °C.

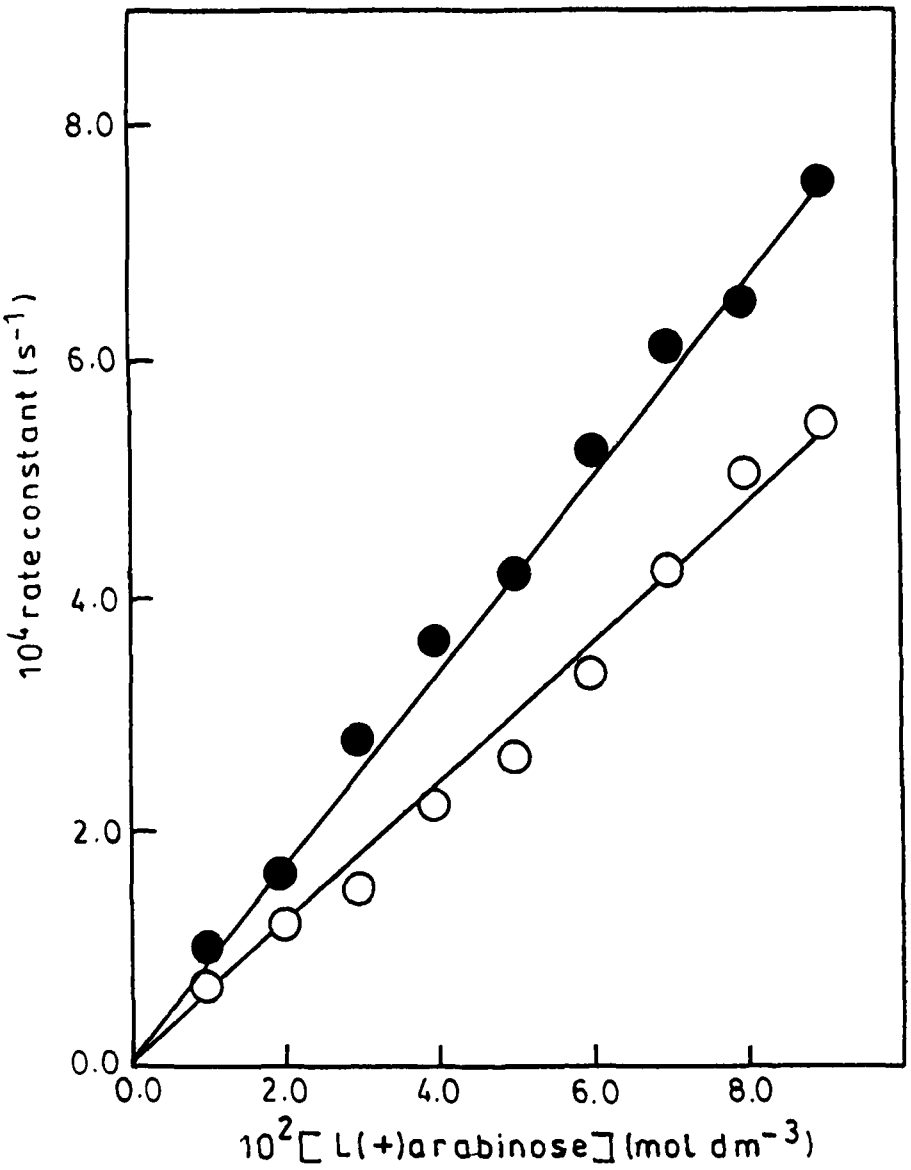


Fig. 3.8: Plots of rate constants *versus* $[L(+)arabinose]_T$ for the oxidation of L(+)arabinose by cerium(IV). *Conditions:* $[Ce(IV)]_T = 1.0 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4]_T = 1.83$ mol dm^{-3}, $[CTAB]_T = 0.0$ (○), 50.0×10^{-4} mol dm^{-3} (●), temperature = 40 °C.

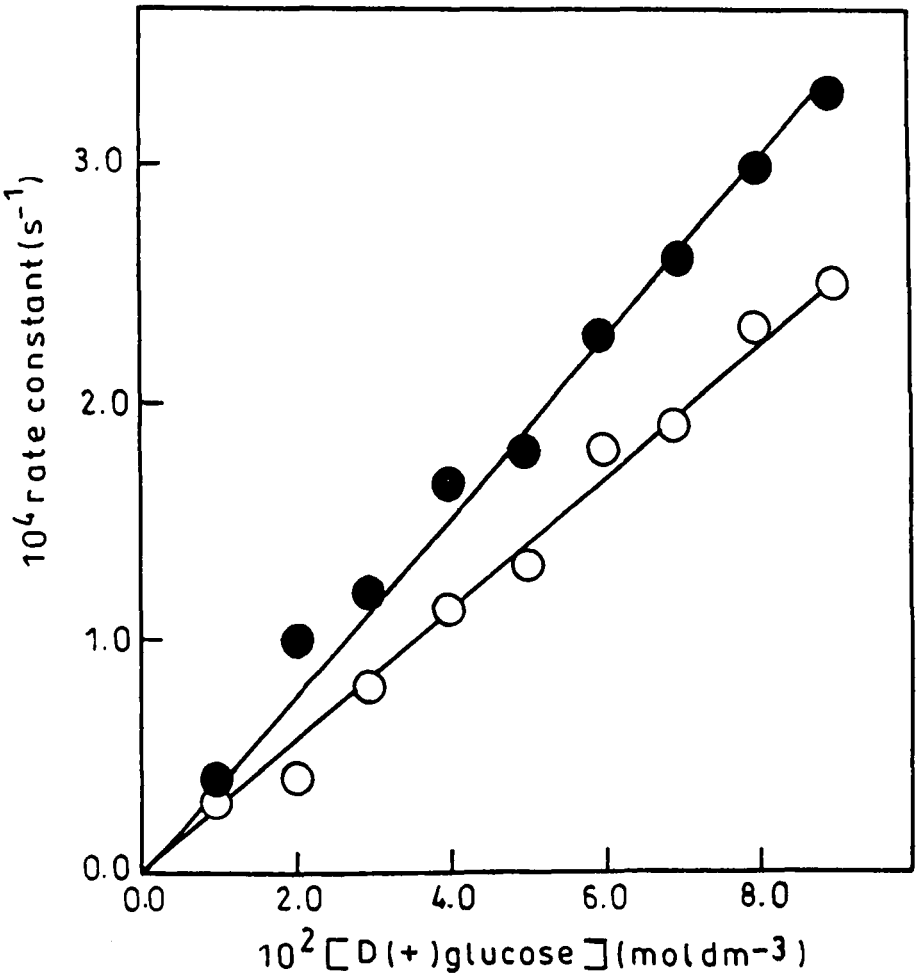


Fig. 3.9: Plots of rate constants *versus* $[D(+)glucose]_T$ for the oxidation of D(+)glucose by cerium(IV). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, $[CTAB]_T$ = 0.0 (○), 50.0 x 10^{-4} mol dm^{-3} (●), temperature = 40 °C.

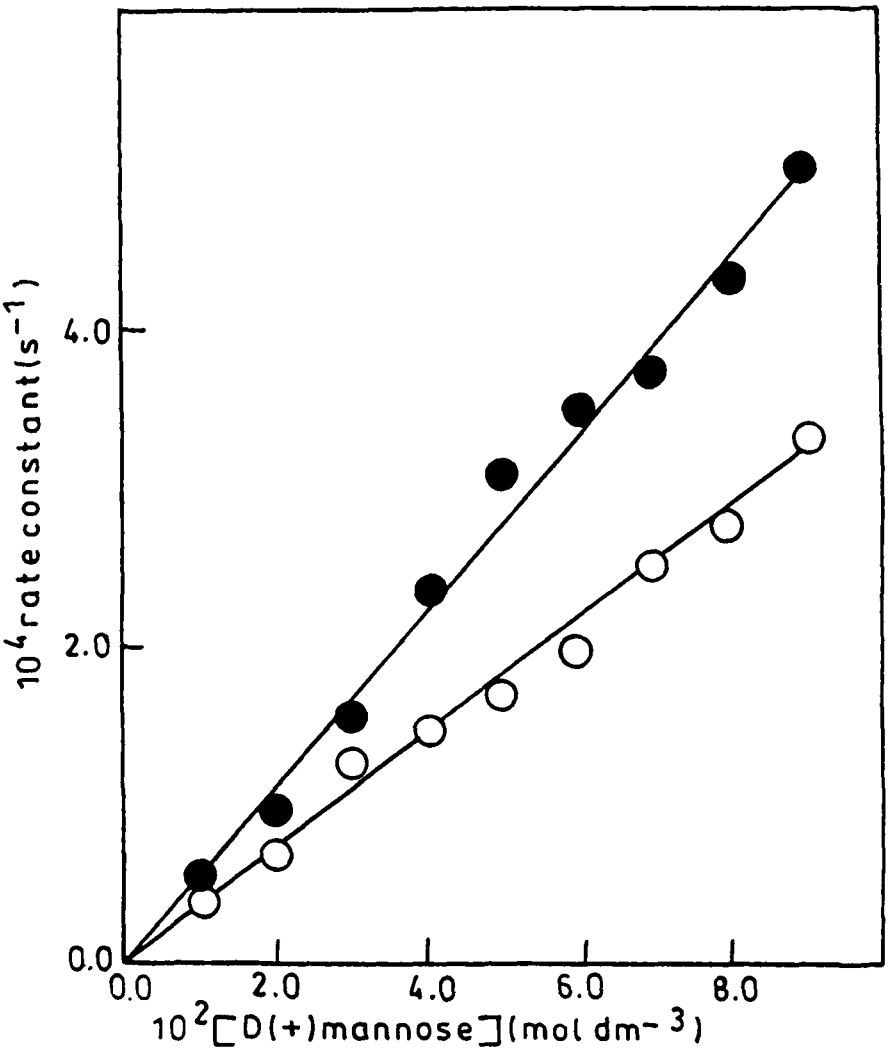


Fig. 3.10: Plots of rate constants *versus* $[D(+)mannose]_T$ for the oxidation of D(+)mannose by cerium(IV). *Conditions:* $[Ce(IV)]_T = 1.0 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, $[CTAB]_T$ = 0.0 (○), 50.0 x 10^{-4} mol dm^{-3} (●), temperature = 40 °C.

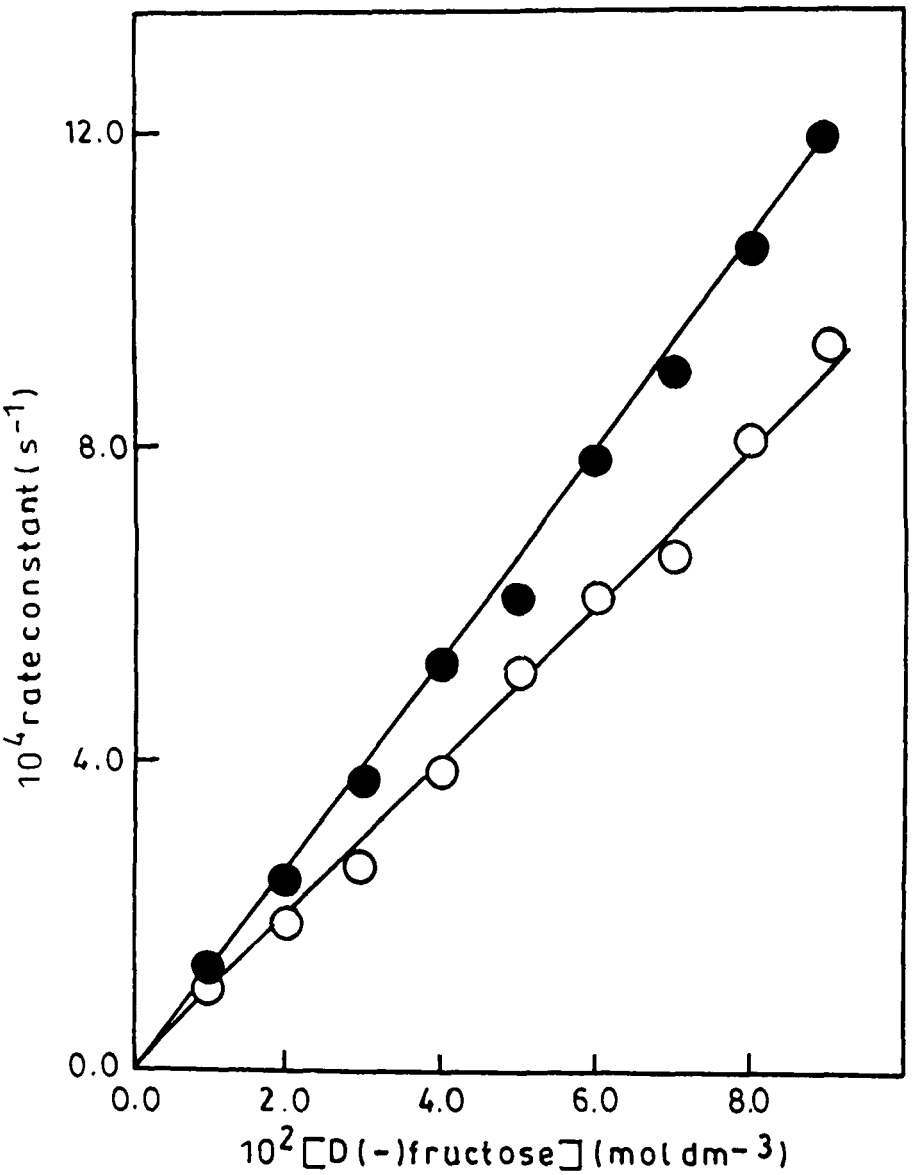


Fig. 3.11: Plots of rate constants *versus* $[D(-)fructose]_T$ for the oxidation of D(–)fructose by cerium(IV). *Conditions:* $[Ce(IV)]_T = 1.0 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4]_T = 1.83$ mol dm^{-3}, $[CTAB]_T = 0.0$ (○), 50.0×10^{-4} mol dm^{-3} (●), temperature = 40 °C.

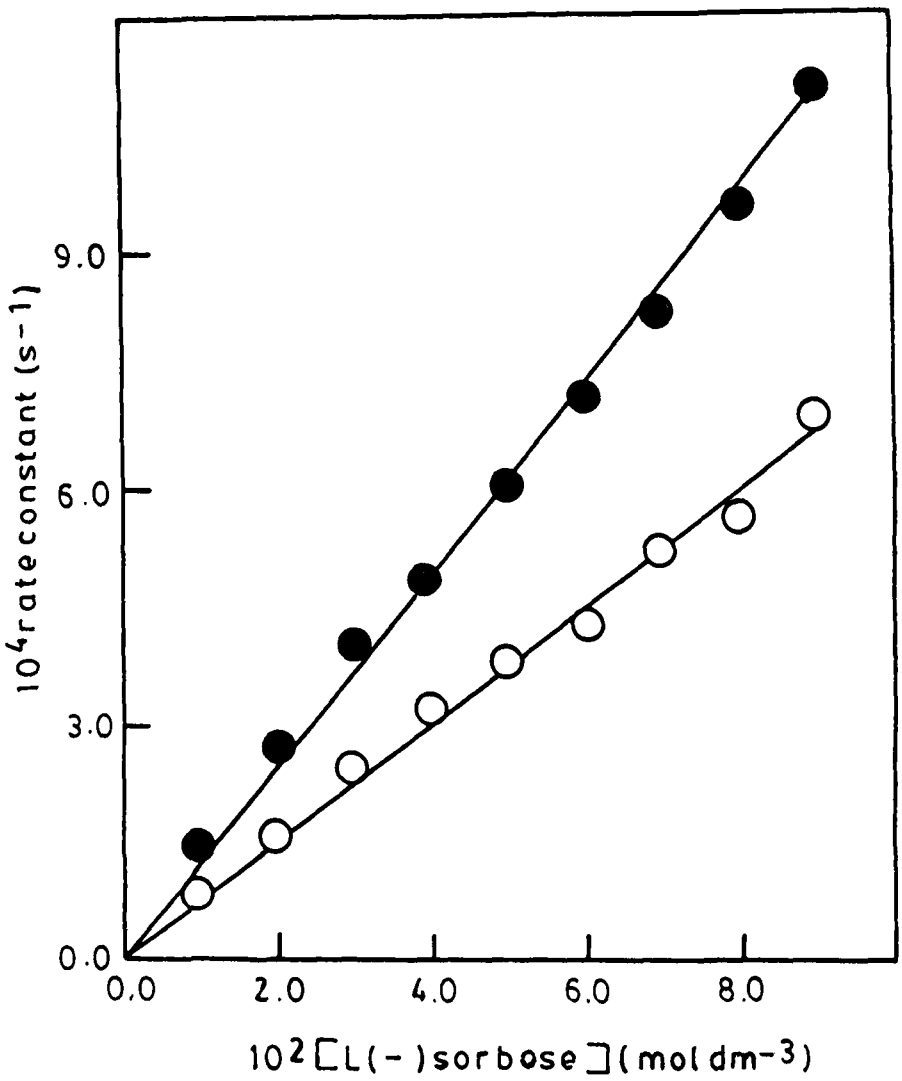


Fig. 3.12: Plots of rate constants *versus* $[L(-)sorbose]_T$ for the oxidation of L(–)sorbose by cerium(IV). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, $[CTAB]_T$ = 0.0 (○), 50.0 x 10^{-4} mol dm^{-3} (●), temperature = 40 °C.

Effect of [H_2SO_4] on the rate

In order to see the role of H_2SO_4, kinetic runs were performed at different [H_2SO_4] (assuming [H_2SO_4] = [H^+]) in the range (0.73–3.67 mol dm^{-3}). At fixed [reductant] (= 4.0 x 10^{-2} mol dm^{-3}), [Ce(IV)] (= 1.0 x 10^{-3} mol dm^{-3}), and temperature (= 40 °C), the rate constants were found to decrease with increase in [H_2SO_4] (Tables 3.13–3.18). Due to involvement of large number of proton dependent equilibria in the cerium(IV),[6–10] the exact computation of [H^+] and interpretation of [H^+] dependence are not possible. However, the inhibition of reaction rate by the addition of H_2SO_4 may be explained as due to the removal of reactive species of cerium(IV).

Effect of [SO_4^{2-}] on the rate

It is well established that cerium(IV) forms a variety of complexes with SO_4^{2-}. Therefore, kinetic experiments were carried out in presence of varying amounts of SO_4^{2-}. It was observed that the rate constant increased with increasing [SO_4^{2-}], indicating involvement of Ce(IV)–sulfato species as the reactive species. The results at different [SO_4^{2-}] at fixed [oxidant], [reductant], [H_2SO_4], and temperature are summarized in Tables 3.19–3.24.

Effect of [HSO_4^-] on the rate

Tables 3.19–3.24 also summarize the effect of [HSO_4^-] on the rates of reactions. The reaction rates are retarded by increase in [HSO_4^-]. The retardation

TABLE 3.13:

Effect of $[H_2SO_4]_T$ on the pseudo-first-order rate constants (k_{obs} or k_Ψ) for the oxidation of D(+)xylose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ $= 1.0 \times 10^{-3}$ mol dm^{-3}
$[D(+)xylose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}
Temperature $= 40$ °C

$[H_2SO_4]_T$	$10^4 k_{obs} / k_\Psi$ (s^{-1})	
(mol dm^{-3})	Aqueous	CTAB[a]
0.73	2.0	turbidity
1.10	2.1	turbidity
1.47	1.8	turbidity
1.83	1.7	2.5
2.20	1.3	2.5
2.57	1.1	2.4
2.94	1.1	2.3
3.30	0.9	2.1
3.67	0.8	2.0

[a]$[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.14:

Effect of $[H_2SO_4]_T$ on the pseudo-first-order rate constants (k_{obs} or k_Ψ) for the oxidation of L(+)arabinose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[L(+)arabinose]_T$ = 4.0×10^{-2} mol dm^{-3}
Temperature = 40 °C

$[H_2SO_4]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\Psi$ (s^{-1})	
	Aqueous	CTAB[a]
0.73	3.5	turbidity
1.10	3.1	turbidity
1.47	2.9	turbidity
1.83	2.2	3.6
2.20	1.9	3.0
2.57	1.7	2.5
2.94	1.7	2.2
3.30	1.3	2.0
3.67	1.1	1.7

[a]$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}

TABLE 3.15:

Effect of $[H_2SO_4]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(+)glucose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ $= 1.0 \times 10^{-3}$ mol dm^{-3}
$[D(+)glucose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}
Temperature $= 40$ °C

$[H_2SO_4]_T$	$10^4 k_{obs} / k_\psi$ (s^{-1})	
(mol dm^{-3})	Aqueous	CTAB[a]
0.73	1.0	turbidity
1.10	1.2	turbidity
1.47	0.9	turbidity
1.83	1.1	1.7
2.20	0.9	1.7
2.57	0.8	1.5
2.94	0.7	1.7
3.30	0.6	1.5
3.67	0.5	1.7

[a]$[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.16:

Effect of $[H_2SO_4]_T$ on the pseudo-first-order rate constants (k_{obs} or k_Ψ) for the oxidation of D(+)mannose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ $= 1.0 \times 10^{-3}$ mol dm^{-3}
$[D(+)mannose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}
Temperature $= 40$ °C

$[H_2SO_4]_T$	$10^4 k_{obs} / k_\Psi$ (s^{-1})	
(mol dm^{-3})	Aqueous	CTAB[a]
0.73	1.5	turbidity
1.10	1.5	turbidity
1.47	1.5	turbidity
1.83	1.5	2.4
2.20	1.2	2.1
2.57	1.0	1.8
2.94	0.8	1.7
3.30	0.7	1.2
3.67	0.5	1.2

[a]$[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.17:

Effect of $[H_2SO_4]_T$ on the pseudo-first-order rate constants (k_{obs} or k_Ψ) for the oxidation of D(−)fructose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[D(-)fructose]_T$ = 4.0×10^{-2} mol dm^{-3}
Temperature = 40 °C

$[H_2SO_4]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\Psi$ (s^{-1})	
	Aqueous	CTAB[a]
0.73	-	turbidity
1.10	6.1	turbidity
1.47	5.7	turbidity
1.83	3.8	5.2
2.20	3.7	4.5
2.57	3.2	3.5
2.94	2.5	2.9
3.30	2.2	2.5
3.67	2.0	2.3

[a]$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}

TABLE 3.18:

Effect of $[H_2SO_4]_T$ on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of L(–)sorbose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[L(-)sorbose]_T$ = 4.0×10^{-2} mol dm^{-3}
Temperature = 40 °C

$[H_2SO_4]_T$ (mol dm^{-3})	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
0.73	4.2	turbidity
1.10	4.6	turbidity
1.47	3.5	turbidity
1.83	3.2	4.7
2.20	2.9	4.1
2.57	2.4	3.6
2.94	2.1	3.2
3.30	1.9	2.7
3.67	1.5	2.6

[a]$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}

TABLE 3.19:

Effect of $[Na_2SO_4]_T$ and $[NaHSO_4]_T$ on the pseudo-first-order rate constants (k_{obs}) for the oxidation of D(+)xylose by cerium(IV) in aqueous medium.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}

$[D(+)xylose]_T$ = 4.0×10^{-2} mol dm^{-3}

$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature = 40 °C

$10^4[Na_2SO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	$10^2[NaHSO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})
0.0	1.7	0.0	1.7
1.0	1.7	5.0	1.7
2.0	1.8	10.0	1.6
4.0	1.8	15.0	1.5
5.0	1.9	20.0	1.3
10.0	2.1	25.0	1.2
		30.0	1.1
		35.0	0.9
		40.0	0.9

TABLE 3.20:

Effect of $[Na_2SO_4]_T$ and $[NaHSO_4]_T$ on the pseudo-first-order rate constants (k_{obs}) for the oxidation of L(+)arabinose by cerium(IV) in aqueous medium.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[L(+)arabinose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}
Temperature = 40 °C

$10^4[Na_2SO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	$10^2[NaHSO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})
0.0	2.2	0.0	2.2
1.0	2.3	5.0	2.0
2.0	2.4	10.0	1.9
4.0	2.9	15.0	1.8
5.0	3.3	20.0	1.6
10.0	4.1	25.0	1.5
		30.0	1.4
		35.0	1.2
		40.0	1.0

TABLE 3.21:

Effect of $[Na_2SO_4]_T$ and $[NaHSO_4]_T$ on the pseudo-first-order rate constants (k_{obs}) for the oxidation of D(+)glucose by cerium(IV) in aqueous medium.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[D(+)glucose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}
Temperature = 40 °C

$10^4[Na_2SO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	$10^2[NaHSO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})
0.0	1.1	0.0	1.1
1.0	1.2	5.0	1.1
2.0	1.5	10.0	1.0
4.0	1.6	15.0	0.9
5.0	1.7	20.0	0.8
		25.0	0.8
		30.0	0.7
		35.0	0.7
		40.0	0.6

TABLE 3.22:

Effect of $[Na_2SO_4]_T$ and $[NaHSO_4]_T$ on the pseudo-first-order rate constants (k_{obs}) for the oxidation of D(+)mannose by cerium(IV) in aqueous medium.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}

$[D(+)mannose]_T$ = 4.0×10^{-2} mol dm^{-3}

$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature = 40 °C

$10^4[Na_2SO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	$10^2[NaHSO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})
0.0	1.5	0.0	1.5
1.0	1.5	5.0	1.5
2.0	1.6	10.0	1.4
4.0	1.7	15.0	1.3
5.0	1.7	20.0	1.3
10.0	1.8	25.0	1.2
		30.0	1.0
		35.0	0.9
		40.0	0.8

TABLE 3.23:

Effect of $[Na_2SO_4]_T$ and $[NaHSO_4]_T$ on the pseudo-first-order rate constants (k_{obs}) for the oxidation of D(–)fructose by cerium(IV) in aqueous medium.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[D(-)fructose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}
Temperature = 40 °C

$10^4[Na_2SO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	$10^2[NaHSO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})
0.0	3.8	0.0	3.8
1.0	3.8	5.0	3.5
2.0	4.0	10.0	3.1
4.0	4.1	15.0	2.8
5.0	4.2	20.0	2.3
		25.0	2.1
		30.0	1.8
		35.0	1.5
		40.0	1.1

TABLE 3.24:

Effect of $[Na_2SO_4]_T$ and $[NaHSO_4]_T$ on the pseudo-first-order rate constants (k_{obs}) for the oxidation of L(–)sorbose by cerium(IV) in aqueous medium.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[L(-)sorbose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}
Temperature = 40 °C

$10^4[Na_2SO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	$10^2[NaHSO_4]_T$ (mol dm^{-3})	10^4k_{obs} (s^{-1})
0.0	3.2	0.0	3.2
1.0	3.2	5.0	3.2
2.0	3.3	10.0	2.9
4.0	3.4	15.0	2.8
5.0	3.5	20.0	2.6
10.0	3.7	25.0	2.2
		30.0	2.2
		35.0	2.0
		40.0	1.9

in the rates with increasing [HSO_4^-] suggests the removal of the reactive species of cerium(IV).

Effect of temperature on the rate

The reactions were performed at different temperatures (30–50 °C). Tables 3.25–3.30 record the values of pseudo-first-order rate constants obtained at the respective temperatures. The Arrhenius plots of log k (*i.e.*, k_{obs} or k_ψ) *versus* 1/T were linear and activation energies (E_a) were evaluated from the slopes of such plots for the oxidation of carbohydrates by cerium(IV). The enthalpies and entropies of activation ($\Delta H^{\#}$ and $\Delta S^{\#}$) were calculated using Eyring equation

$$k = (k_B T/h) \exp (\Delta S^{\#}/R) \exp (-\Delta H^{\#}/RT) \qquad (3.2)$$

where the symbols have their usual meaning. Tables 3.25–3.30 also record the thermodynamic parameters.

Effect of [surfactant] on the rate

Several redox reactions in the micellar media are influenced by the hydrophobic and electrostatic forces and, for a given set of reactions, the observed rate depends on the extent of association between the reactants and micellar aggregates. Therefore, in order to see the role of surfactants, a series of kinetic runs were performed in presence of varying amounts of sodium dodecyl

TABLE 3.25:

Effect of temperature on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(+)xylose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ $= 1.0 \times 10^{-3}$ mol dm^{-3}

$[D(+)xylose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}

$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}

Temperature	$10^4 k_{obs} / k_\psi (s^{-1})$	
(°C)	Aqueous	CTAB[a]
30	0.5	0.8
35	0.9	1.4
40	1.7	2.5
45	3.0	4.1
50	5.6	7.5
Parameters		
E_a (kJmol^{-1})	99	93
$\Delta H^{\#}$ (kJmol^{-1})	96	90
$\Delta S^{\#}$ (JK^{-1}mol^{-1})	−10	−27

[a]$[CTAB]_T$ $= 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.26:

Effect of temperature on the pseudo-first-order rate constants (k_{obs} or k_Ψ) for the oxidation of L(+)arabinose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[L(+)arabinose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature	$10^4 k_{obs} / k_\Psi (s^{-1})$	
(°C)	Aqueous	CTAB[a]
30	0.8	1.0
35	1.5	1.8
40	2.2	3.6
45	5.2	6.0
50	6.8	8.6
Parameters		
E_a ($kJmol^{-1}$)	98	89
$\Delta H^{\#}$ ($kJmol^{-1}$)	96	86
$\Delta S^{\#}$ ($JK^{-1}mol^{-1}$)	−17	−35

[a]$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}

TABLE 3.27:

Effect of temperature on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(+)glucose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T = 1.0 \times 10^{-3}$ mol dm^{-3}
$[D(+)glucose]_T = 4.0 \times 10^{-2}$ mol dm^{-3}
$[H_2SO_4]_T = 1.83$ mol dm^{-3}

Temperature (°C)	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
30	0.3	0.6
35	0.9	1.2
40	1.1	1.7
45	2.0	2.7
50	3.3	4.3
Parameters		
E_a (kJmol^{-1})	92	88
$\Delta H^{\#}$ (kJmol^{-1})	89	85
$\Delta S^{\#}$ (JK^{-1}mol^{-1})	–54	–84

[a]$[CTAB]_T = 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.28:

Effect of temperature on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(+)mannose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ $= 1.0 \times 10^{-3}$ mol dm^{-3}

$[D(+)mannose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}

$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}

Temperature	$10^4 k_{obs} / k_\psi$ (s^{-1})	
(°C)	Aqueous	CTAB[a]
30	0.4	0.7
35	0.8	1.4
40	1.5	2.4
45	2.4	3.3
50	3.8	4.8
Parameters		
E_a (kJmol^{-1})	94	79
$\Delta H^{\#}$ (kJmol^{-1})	91	76
$\Delta S^{\#}$ (JK^{-1}mol^{-1})	-28	-73

[a]$[CTAB]_T$ $= 50.0 \times 10^{-4}$ mol dm^{-3}

TABLE 3.29:

Effect of temperature on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of D(–)fructose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[D(-)fructose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature (°C)	$10^4 k_{obs} / k_\psi$ (s^{-1})	
	Aqueous	CTAB[a]
30	1.1	1.7
35	2.5	3.0
40	3.8	5.2
45	8.0	9.0
50	12.2	14.1
Parameters		
E_a ($kJmol^{-1}$)	99	87
$\Delta H^{\#}$ ($kJmol^{-1}$)	96	85
$\Delta S^{\#}$ ($JK^{-1}mol^{-1}$)	–17	–38

[a]$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}

TABLE 3.30:

Effect of temperature on the pseudo-first-order rate constants (k_{obs} or k_ψ) for the oxidation of L(–)sorbose by cerium(IV) in the absence and presence of CTAB.

Conditions: $[Ce(IV)]_T$ $= 1.0 \times 10^{-3}$ mol dm^{-3}

$[L(-)sorbose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}

$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}

Temperature	$10^4 k_{obs} / k_\psi$ (s^{-1})	
(°C)	Aqueous	CTAB[a]
30	1.0	1.7
35	1.8	2.5
40	3.2	4.8
45	5.1	7.7
50	9.0	13.2
Parameters		
E_a (kJmol^{-1})	90	86
$\Delta H^{\#}$ (kJmol^{-1})	87	83
$\Delta S^{\#}$ (JK^{-1}mol^{-1})	–34	–43

[a]$[CTAB]_T$ $= 50.0 \times 10^{-4}$ mol dm^{-3}

sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) at constant [Ce(IV)] (= 1.0 x 10^{-3} mol dm^{-3}), [carbohydrate] (= 4.0 x 10^{-2} mol dm^{-3}), [H_2SO_4] (= 1.83 mol dm^{-3}), and temperature (= 40 °C). The rate constants are summarized in Tables 3.31 – 3.36. It is observed that the rate constants increase with increase in [CTAB] but SDS has no effect (Figs. 3.13–3.18).

In order to see whether the bromide ion is capable of a reaction with cerium(IV) under our kinetic conditions, some experiments were also performed in the absence of carbohydrates (cerium(IV) + CTAB + H_2SO_4). The absorbance of cerium(IV) remained constant for the entire range of [CTAB] used in the kinetic experiments (Figs. 3.1–3.6, A). This suggests that the oxidation of bromide ion by cerium(IV) is not involved even as a side reaction in the carbohydrate oxidation by cerium(IV) in presence of CTAB. Furthermore, a series of kinetic experiments performed with varying [Br^-] ((10.0 to 50.0) x 10^{-4} mol dm^{-3}) at constant [H_2SO_4] = 1.83 mol dm^{-3}, [Ce(IV)] = 1.0 x 10^{-3} mol dm^{-3}, and temperature = 40 °C showed constancy of absorbance upto 90 min (typical time required for complete oxidation of carbohydrates under our kinetic conditions). These results confirm that there is no reduction of cerium(IV) by bromide ion.

Effect of [oxidant], [reductant], [H_2SO_4] and temperature on the rate in micellar medium

To see the effects of [oxidant], [reductant], [H_2SO_4] and temperature, and to further confirm the mechanism (*vide infra*), a series of kinetic experiments

TABLE 3.31:

Effect of $[surfactant]_T$ on the pseudo-first-order rate constants (k_ψ) for the oxidation of D(+)xylose by cerium(IV).

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}

$[D(+)xylose]_T$ = 4.0×10^{-2} mol dm^{-3}

$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature = 40 °C

$10^4[surfactant]_T$ (mol dm^{-3})	$10^4 k_\psi$ (s^{-1})		$10^4 k_{\psi cal}$ (s^{-1})
	CTAB	SDS	CTAB
0.0	1.7	1.7	-
10.0	1.9	1.6	1.9
20.0	2.1	1.6	2.1
30.0	2.2	1.6	2.2
40.0	2.5	1.7	2.4
50.0	2.5	1.7	2.5
75.0	2.8	1.6	2.7
100.0	2.8	1.6	2.9
125.0	3.0	1.7	3.0
150.0	3.1	1.6	3.1

TABLE 3.32:

Effect of $[surfactant]_T$ on the pseudo-first-order rate constants (k_ψ) for the oxidation of L(+)arabinose by cerium(IV).

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}

$[L(+)arabinose]_T$ = 4.0×10^{-2} mol dm^{-3}

$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature = 40 °C

$10^4[surfactant]_T$ (mol dm^{-3})	$10^4 k_\psi$ (s^{-1})		$10^4 k_{\psi cal}$ (s^{-1})
	CTAB	SDS	CTAB
0.0	2.2	2.2	-
10.0	2.3	-	2.6
20.0	2.9	-	2.9
30.0	3.1	-	3.1
40.0	3.3	-	3.3
50.0	3.6	2.1	3.5
75.0	3.7	2.3	3.7
100.0	3.7	2.1	3.9
125.0	4.0	-	4.1
150.0	4.2	2.2	4.2

oxidation of D(+)glucose by cerium(IV).

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}

$[D(+)glucose]_T$ = 4.0×10^{-2} mol dm^{-3}

$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature = 40 °C

$10^4[surfactant]_T$	$10^4 k_\psi$ (s^{-1})		$10^4 k_{\psi cal}$ (s^{-1})
(mol dm^{-3})	CTAB	SDS	CTAB
0.0	1.1	1.1	-
10.0	1.2	-	1.2
20.0	1.3	1.1	1.3
30.0	1.4	1.2	1.4
40.0	1.4	-	1.4
50.0	1.7	1.1	1.5
75.0	1.7	-	1.7
100.0	1.8	1.1	1.8
125.0	1.9	-	1.9
150.0	2.0	1.0	2.0

TABLE 3.34:

Effect of $[surfactant]_T$ on the pseudo-first-order rate constants (k_Ψ) for the oxidation of D(+)mannose by cerium(IV).

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}

$[D(+)mannose]_T$ = 4.0×10^{-2} mol dm^{-3}

$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature = 40 °C

$10^4[surfactant]_T$ (mol dm^{-3})	$10^4 k_\Psi$ (s^{-1})		$10^4 k_{\Psi cal}$ (s^{-1})
	CTAB	SDS	CTAB
0.0	1.5	1.5	-
10.0	1.7	1.5	1.7
20.0	1.8	1.5	1.8
30.0	2.1	1.4	2.0
40.0	2.2	-	2.1
50.0	2.4	1.5	2.3
75.0	2.6	-	2.5
100.0	2.7	1.5	2.7
125.0	2.8	1.5	2.9
150.0	2.9	1.5	3.0

TABLE 3.35:

Effect of $[surfactant]_T$ on the pseudo-first-order rate constants (k_Ψ) for the oxidation of D(−)fructose by cerium(IV).

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}

$[D(-)fructose]_T$ = 4.0×10^{-2} mol dm^{-3}

$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature = 40 °C

$10^4[surfactant]_T$ (mol dm^{-3})	$10^4 k_\Psi$ (s^{-1})		$10^4 k_{\Psi cal}$ (s^{-1})
	CTAB	SDS	CTAB
0.0	3.8	3.8	-
10.0	4.4	-	4.2
20.0	4.6	-	4.6
30.0	4.8	-	4.8
40.0	5.0	-	5.0
50.0	5.2	3.8	5.2
75.0	5.4	3.8	5.4
100.0	5.6	4.2	5.6
125.0	5.8	-	5.8
150.0	6.0	3.8	5.9

TABLE 3.36:

Effect of $[surfactant]_T$ on the pseudo-first-order rate constants (k_Ψ) for the oxidation of L(–)sorbose by cerium(IV).

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[L(-)sorbose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}
Temperature = 40 °C

$10^4[surfactant]_T$	$10^4 k_\Psi$ (s^{-1})		$10^4 k_{\Psi cal}$ (s^{-1})
(mol dm^{-3})	CTAB	SDS	CTAB
0.0	3.2	3.2	-
10.0	3.6	-	3.6
20.0	4.0	-	3.9
30.0	4.2	-	4.2
40.0	4.4	-	4.5
50.0	4.7	3.2	4.7
75.0	5.2	3.2	5.1
100.0	5.5	3.1	5.4
125.0	5.7	-	5.6
150.0	6.0	3.1	5.8

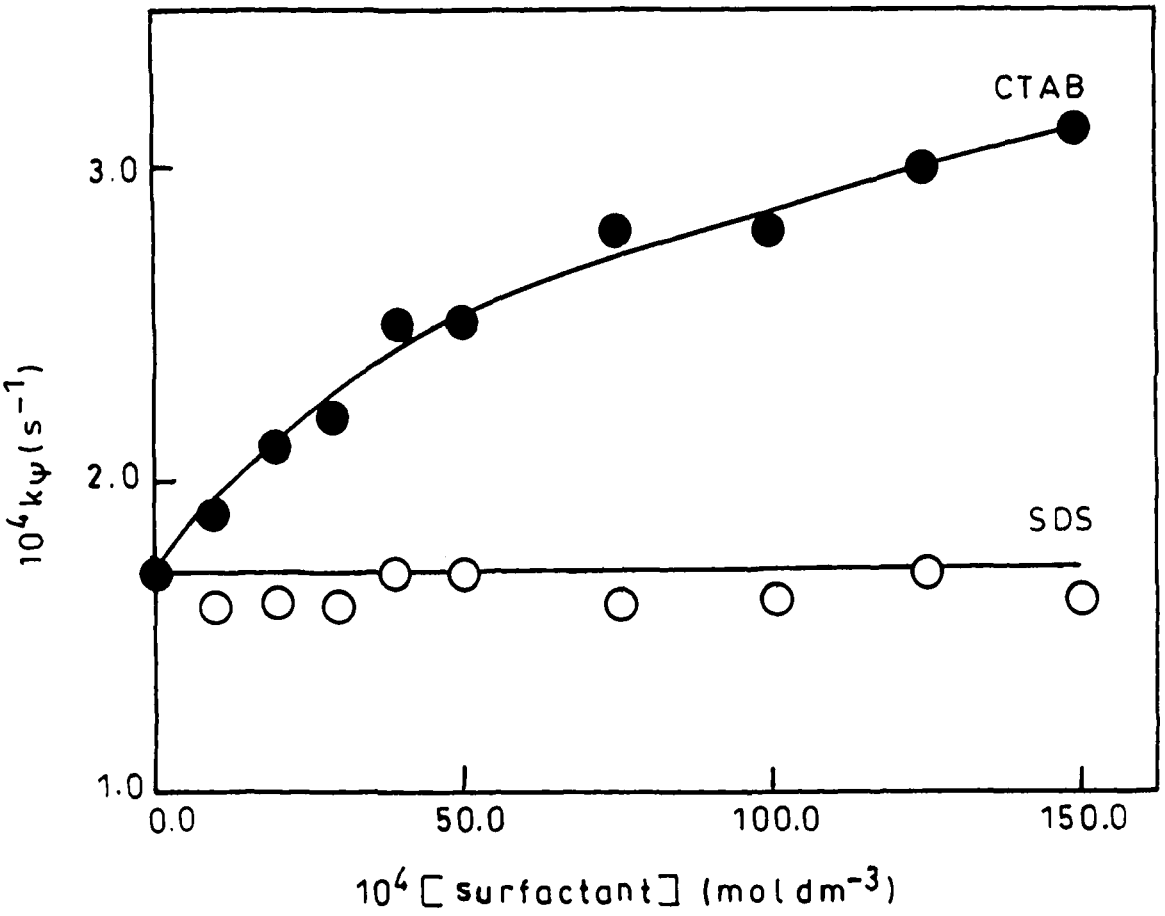


Fig. 3.13: Effect of $[surfactant]_T$ on the rate constant for the oxidation of D(+)xylose by cerium(IV). *Conditions:* $[Ce(IV)]_T = 1.0 \times 10^{-3}$ mol dm^{-3}, $[D(+)xylose]_T = 4.0 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4]_T = 1.83$ mol dm^{-3}, temperature = 40 °C.

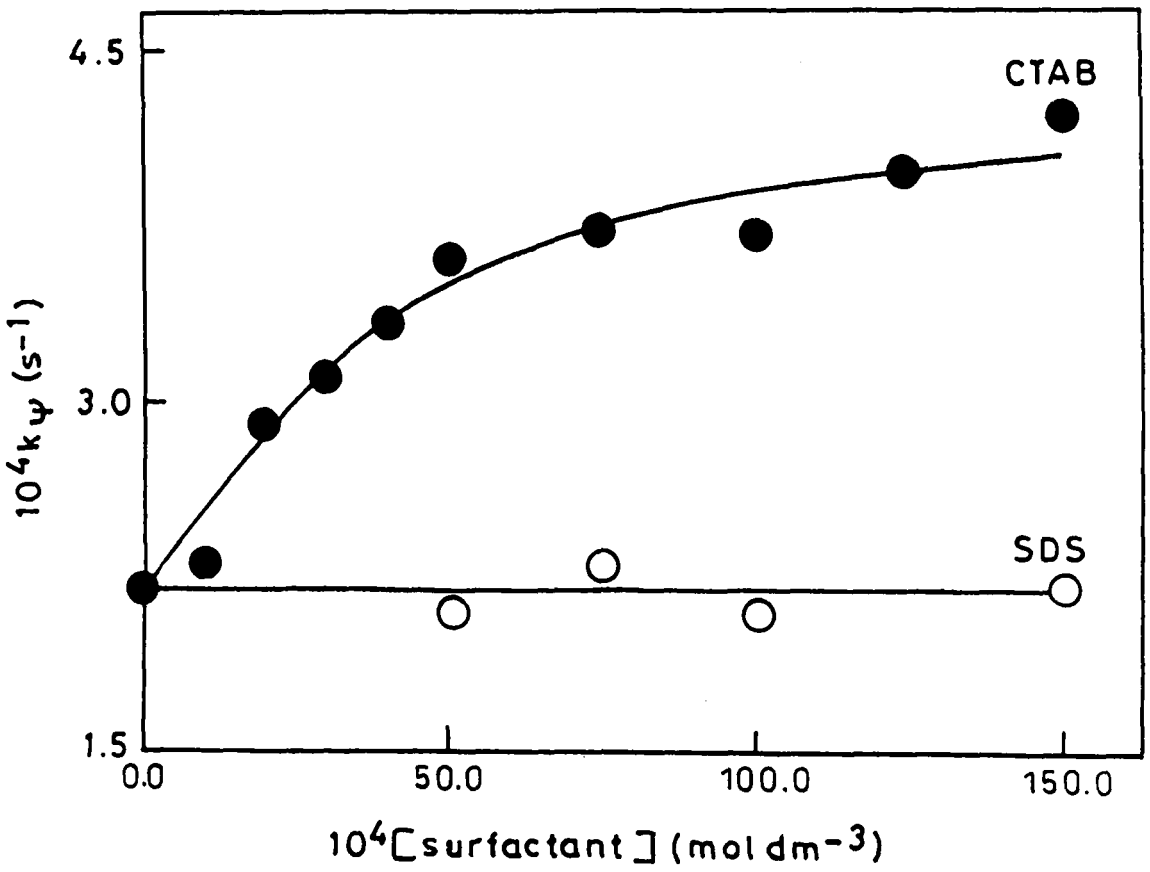


Fig. 3.14: Effect of $[surfactant]_T$ on the rate constant for the oxidation of L(+)arabinose by cerium(IV). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[L(+)arabinose]_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

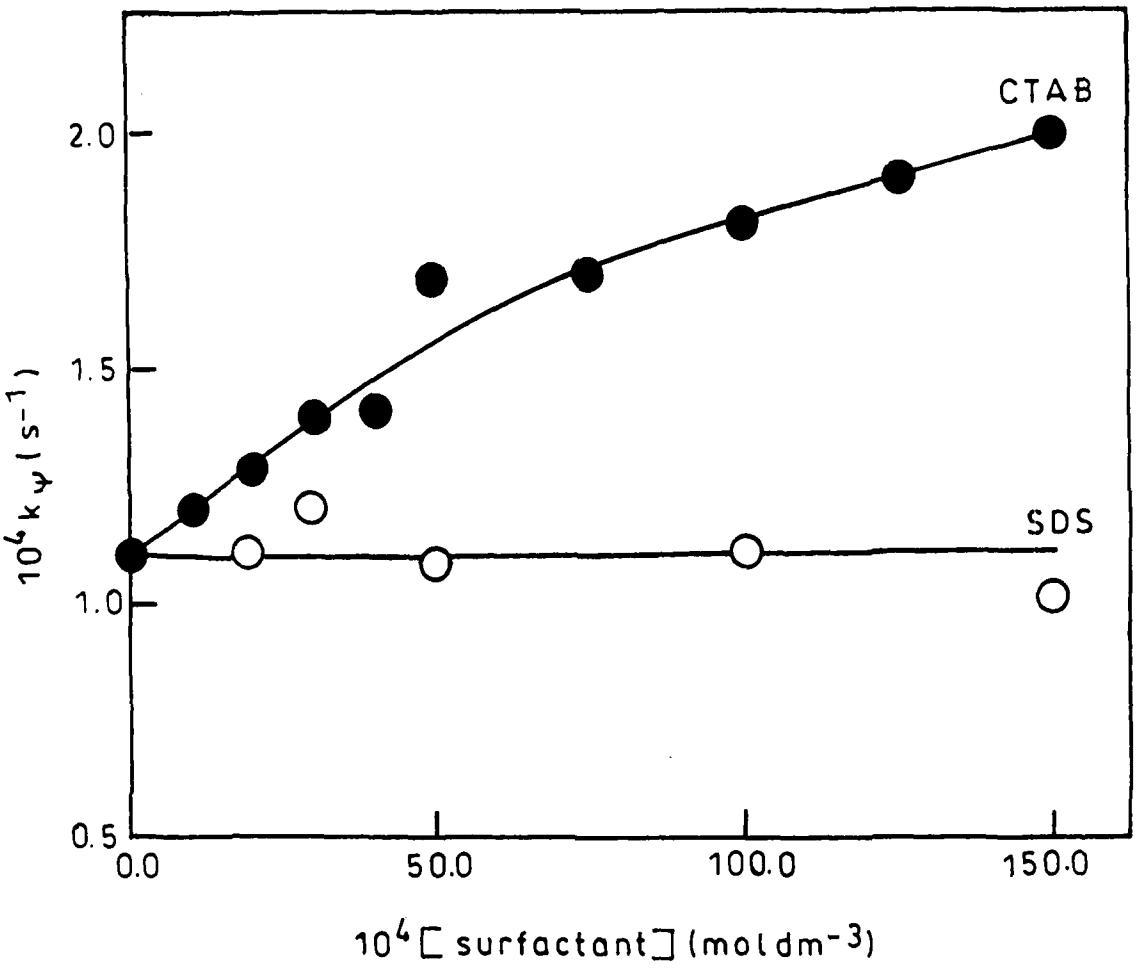


Fig. 3.15: Effect of $[surfactant]_T$ on the rate constant for the oxidation of D(+)glucose by cerium(IV). *Conditions:* $[Ce(IV)]_T = 1.0 \times 10^{-3}$ mol dm^{-3}, $[D(+)glucose]_T = 4.0 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4]_T = 1.83$ mol dm^{-3}, temperature = 40 °C.

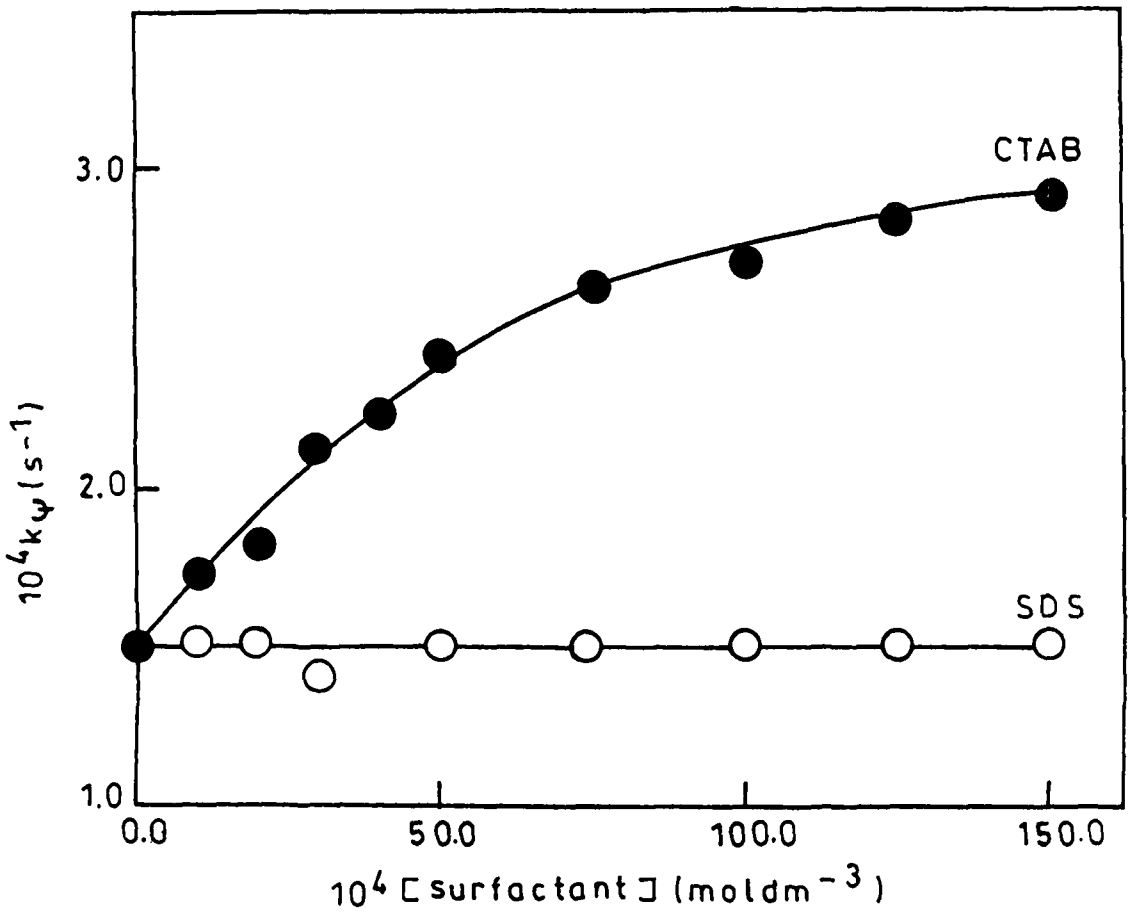


Fig. 3.16: Effect of $[surfactant]_T$ on the rate constant for the oxidation of D(+)mannose by cerium(IV). *Conditions:* $[Ce(IV)]_T = 1.0 \times 10^{-3}$ mol dm^{-3}, $[D(+)mannose]_T = 4.0 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4]_T = 1.83$ mol dm^{-3}, temperature = 40 °C.

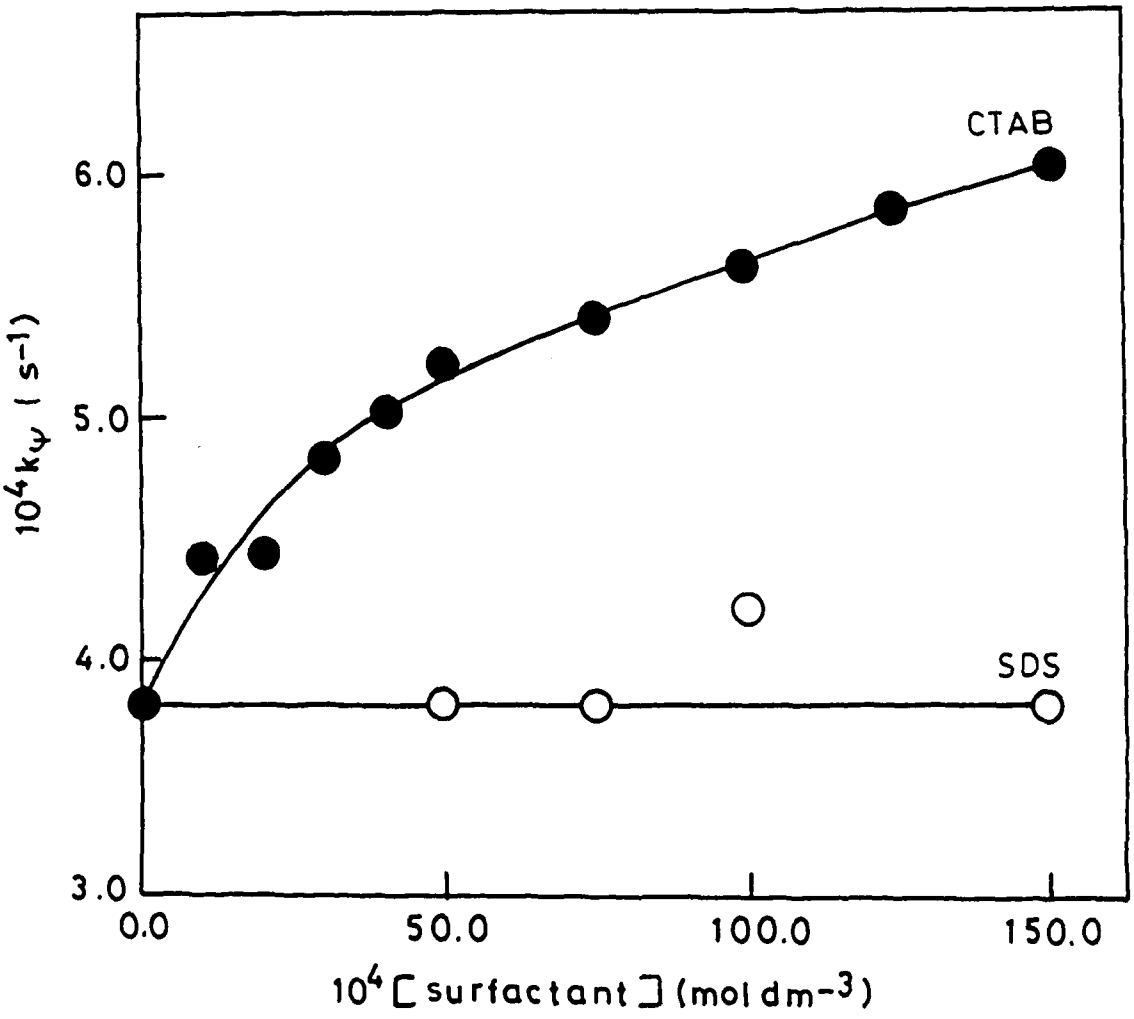


Fig. 3.17: Effect of $[surfactant]_T$ on the rate constant for the oxidation of D(−)fructose by cerium(IV). *Conditions:* $[Ce(IV)]_T = 1.0 \times 10^{-3}$ mol dm^{-3}, $[D(-)fructose]_T = 4.0 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4]_T = 1.83$ mol dm^{-3}, temperature = 40 °C.

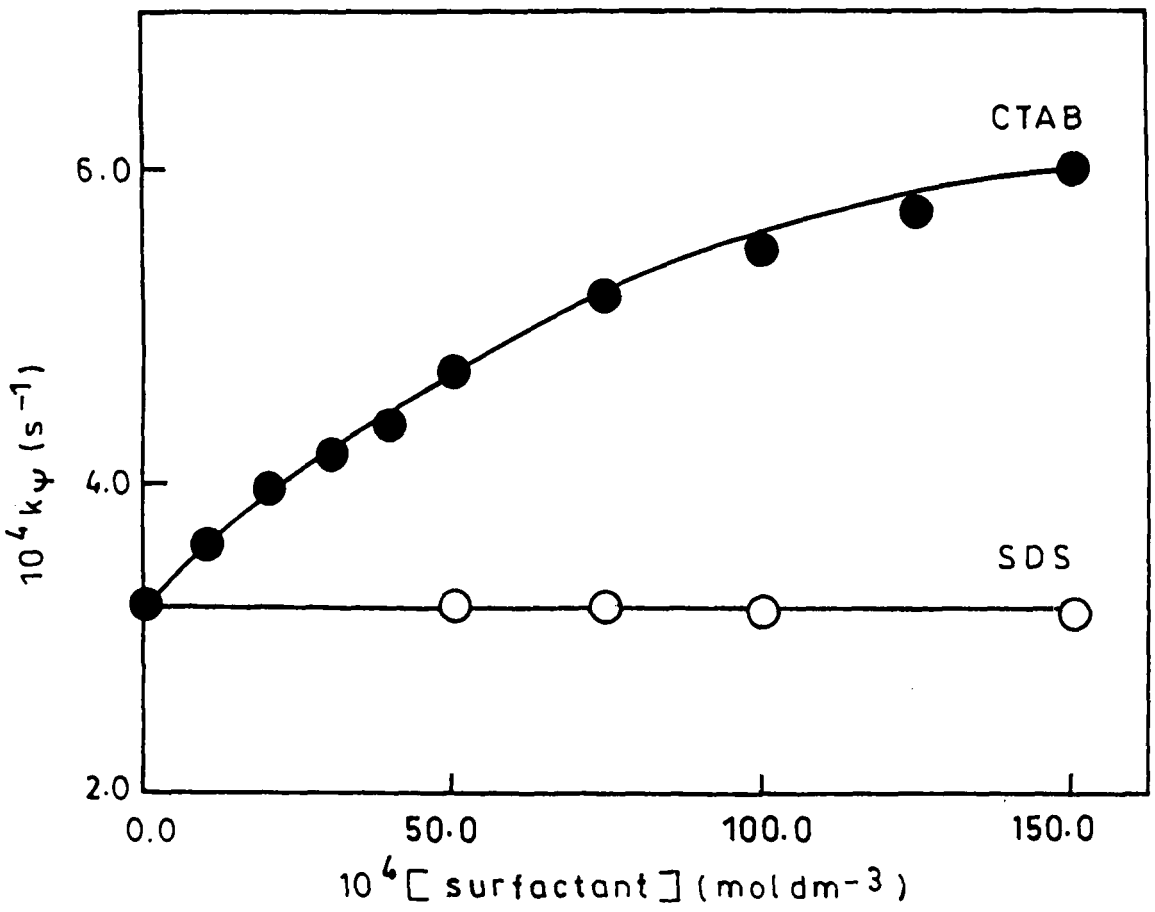


Fig. 3.18: Effect of $[surfactant]_T$ on the rate constant for the oxidation of L(–)sorbose by cerium(IV). *Conditions:* $[Ce(IV)]_T = 1.0 \times 10^{-3}$ mol dm^{-3}, $[L(-)sorbose]_T = 4.0 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4]_T = 1.83$ mol dm^{-3}, temperature = 40 °C.

were performed at constant [CTAB]. The k_ψ – values, obtained as functions of the above variables, are summarized in Tables 3.1–3.18 and 3.25–3.30. The effect of [carbohydrate] on the k_ψ in the presence of CTAB are shown in Figs. 3.7–3.12. The behavior on variation of [oxidant], [reductant], [H_2SO_4], and temperature was identical to the aqueous medium and the kinetics follow the same pattern, *i.e.*, first-order in [Ce(IV)] and [carbohydrate] and inverse order in [H_2SO_4]. These observations undoubtedly establish that the mechanism of oxidation of the carbohydrates by cerium(IV) in presence of CTAB remains the same as in aqueous medium.

Effect of [salt] on the rate in micellar medium

The effect of added salts on the rate were also explored because salts, as additives, in micellar systems acquire a special place due to their ability to induce structural changes which may, in turn, modify the substrate–surfactant interactions. The salt effect on the micelle catalyzed cerium(IV)–carbohydrate reactions were studied in presence of CTAB micelles at 40 °C.

The observed data in the presence of inorganic salts (Na_2SO_4, $NaNO_3$ and NaCl) are recorded in Tables 3.37–3.42 and shown graphically in Figs. 3.19–3.24.

TABLE 3.37:

Effect of $[salt]_T$ on the pseudo-first-order rate constants (k_ψ) for the oxidation of D(+)xylose by cerium(IV) in presence of CTAB.

Conditions: $[Ce(IV)]_T$ $= 1.0 \times 10^{-3}$ mol dm^{-3}
$[D(+)xylose]_T$ $= 4.0 \times 10^{-2}$ mol dm^{-3}
$[H_2SO_4]_T$ $= 1.83$ mol dm^{-3}
$[CTAB]_T$ $= 50.0 \times 10^{-4}$ mol dm^{-3}
Temperature $= 40$ °C

$10^2[salt]_T$	$10^4 k_\psi$ (s^{-1})		
(mol dm^{-3})	Na_2SO_4	$NaNO_3$	NaCl
0.0	2.5	2.5	2.5
1.0	2.5	2.5	2.5
2.5	2.4	2.4	2.5
5.0	2.1	2.3	2.5
7.5	2.0	2.2	2.4
10.0	1.8	2.1	2.3
12.5	1.8	2.1	2.2
15.0	1.7	2.0	2.2
20.0	1.5	1.9	2.1

TABLE 3.38:

Effect of $[salt]_T$ on the pseudo-first-order rate constants (k_Ψ) for the oxidation of L(+)arabinose by cerium(IV) in presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[L(+)arabinose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}
$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}
Temperature = 40 °C

$10^2[salt]_T$ (mol dm^{-3})	$10^4 k_\Psi$ (s^{-1})		
	Na_2SO_4	$NaNO_3$	NaCl
0.0	3.6	3.6	3.6
1.0	3.5	3.6	3.6
2.5	3.3	3.5	3.5
5.0	3.1	3.3	3.4
7.5	2.8	3.2	3.3
10.0	2.7	3.1	3.2
12.5	2.6	2.9	3.2
15.0	2.4	2.8	3.1
20.0	2.2	2.6	2.9

TABLE 3.39:

Effect of $[salt]_T$ on the pseudo-first-order rate constants (k_Ψ) for the oxidation of D(+)glucose by cerium(IV) in presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[D(+)glucose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}
$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}
Temperature = 40 °C

$10^2[salt]_T$ (mol dm^{-3})	$10^4 k_\Psi$ (s^{-1})		
	Na_2SO_4	$NaNO_3$	NaCl
0.0	1.7	1.7	1.7
1.0	1.7	1.7	1.7
2.5	1.5	1.6	1.7
5.0	1.5	1.5	1.6
7.5	1.4	1.4	1.6
10.0	1.2	1.4	1.5
12.5	1.2	1.3	1.5
15.0	1.0	1.3	1.4
20.0	1.0	1.2	1.4

TABLE 3.40:

Effect of $[salt]_T$ on the pseudo-first-order rate constants (k_Ψ) for the oxidation of D(+)mannose by cerium(IV) in presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[D(+)mannose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}
$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}
Temperature = 40 °C

$10^2[salt]_T$	$10^4 k_\Psi$ (s^{-1})		
(mol dm^{-3})	Na_2SO_4	$NaNO_3$	NaCl
0.0	2.4	2.4	2.4
1.0	2.2	2.2	2.4
2.5	2.1	2.1	2.4
5.0	1.9	2.1	2.4
7.5	1.7	2.0	2.2
10.0	1.5	1.8	2.2
12.5	1.5	1.8	2.1
15.0	1.4	1.7	2.1
20.0	1.3	1.6	1.9

TABLE 3.41:

Effect of $[salt]_T$ on the pseudo-first-order rate constants (k_Ψ) for the oxidation of D(–)fructose by cerium(IV) in presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[D(-)fructose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}
$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}
Temperature = 40 °C

$10^2[salt]_T$	$10^4 k_\Psi$ (s^{-1})		
(mol dm^{-3})	Na_2SO_4	$NaNO_3$	NaCl
0.0	5.2	5.2	5.2
1.0	5.1	5.2	5.2
2.5	5.0	5.1	5.1
5.0	4.7	4.9	5.0
7.5	4.2	4.7	4.8
10.0	3.8	4.6	4.8
12.5	3.5	4.3	4.5
15.0	3.2	4.1	4.3
20.0	2.9	3.8	4.1

TABLE 3.42:

Effect of $[salt]_T$ on the pseudo-first-order rate constants (k_Ψ) for the oxidation of L(–)sorbose by cerium(IV) in presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[L(-)sorbose]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}
$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}
Temperature = 40 °C

$10^2[salt]_T$	$10^4 k_\Psi$ (s^{-1})		
(mol dm^{-3})	Na_2SO_4	$NaNO_3$	NaCl
0.0	4.7	4.7	4.7
1.0	4.2	4.4	4.5
2.5	4.0	4.2	4.3
5.0	3.8	4.2	4.3
7.5	3.4	4.1	4.1
10.0	3.2	4.0	4.0
12.5	3.0	3.8	4.0
15.0	2.8	3.8	3.8
20.0	2.6	3.5	3.8

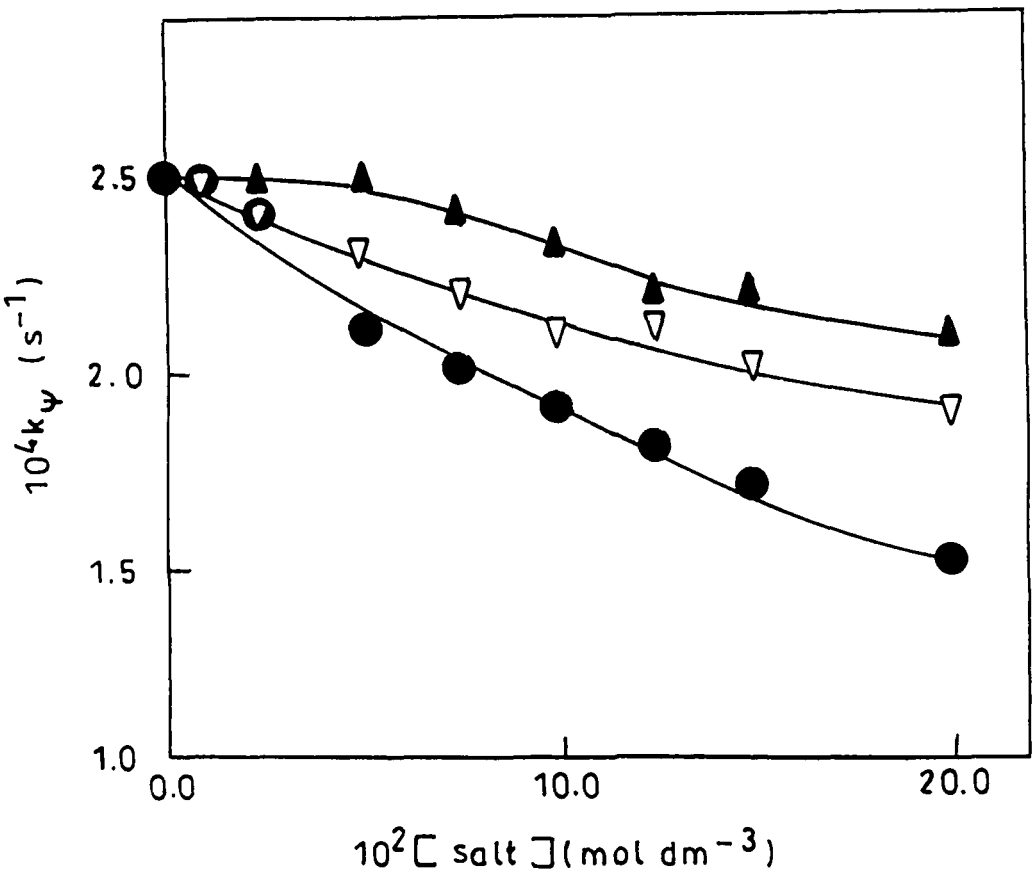


Fig. 3.19: Effect of $[salt]_T$ (Na_2SO_4 (●), $NaNO_3$ (▽) and NaCl (▲)) on the rate of oxidation of D(+)xylose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[D(+)xylose]_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

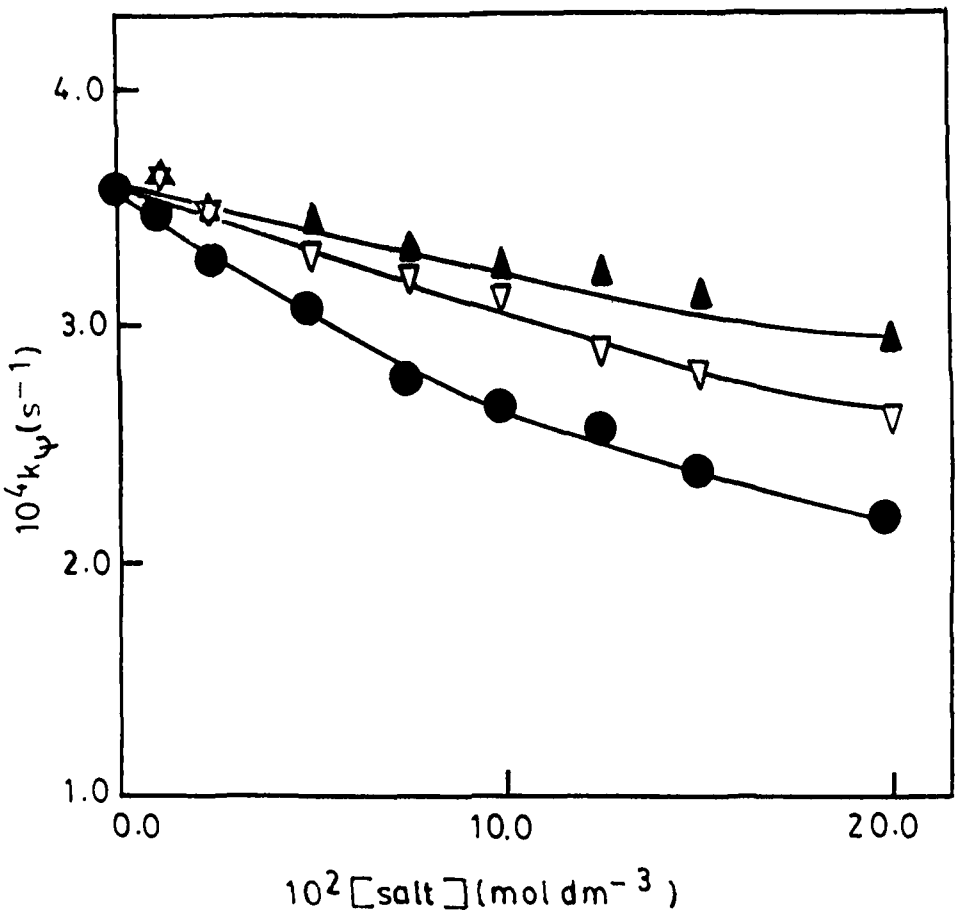


Fig. 3.20: Effect of $[salt]_T$ (Na_2SO_4 (●), $NaNO_3$ (▽) and NaCl (▲)) on the rate of oxidation of L(+)arabinose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, [L(+)arabinose]$_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

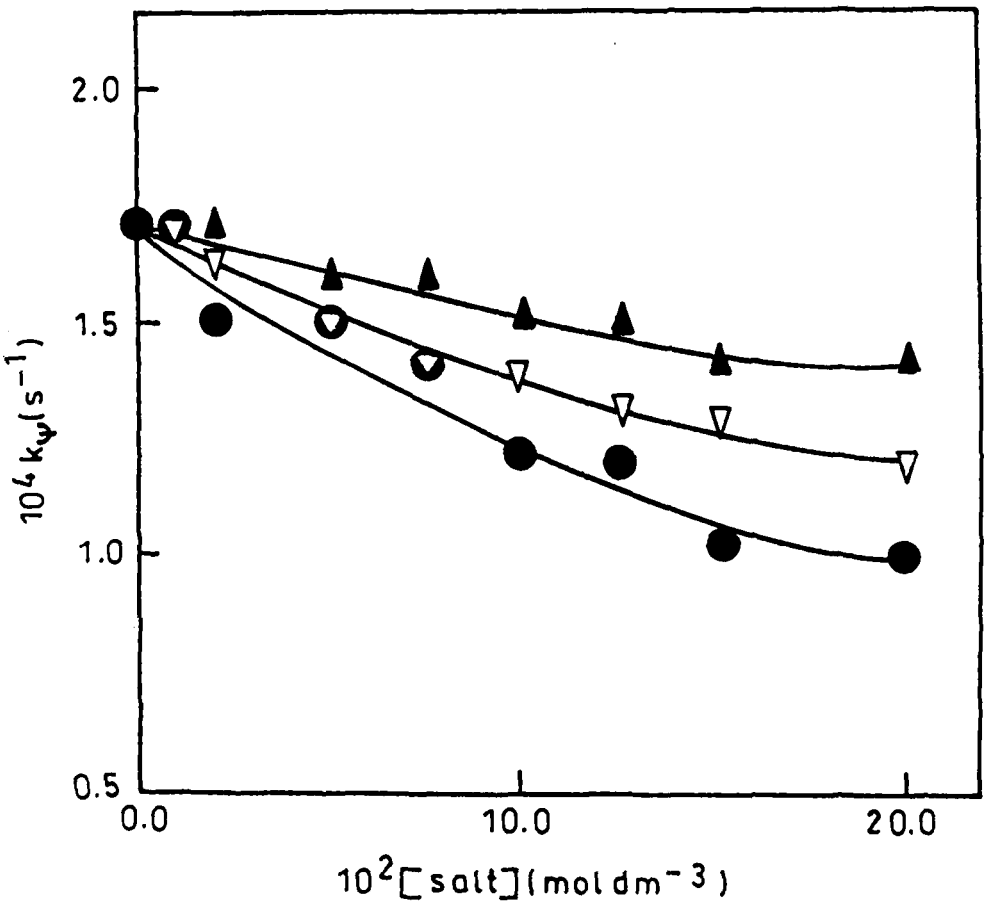


Fig. 3.21: Effect of $[salt]_T$ (Na_2SO_4 (●), $NaNO_3$ (▽) and NaCl (▲)) on the rate of oxidation of D(+)glucose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[D(+)glucose]_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

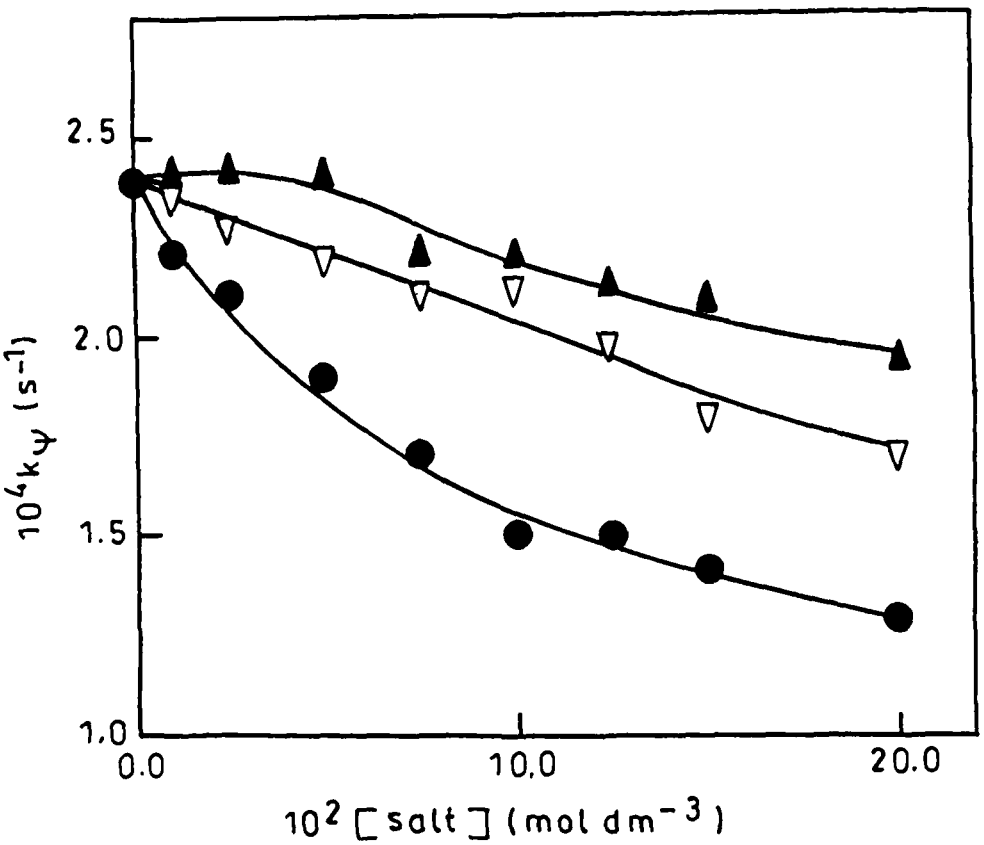


Fig. 3.22: Effect of $[salt]_T$ (Na_2SO_4 (●), $NaNO_3$ (▽) and NaCl (▲)) on the rate of oxidation of D(+)mannose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[D(+)mannose]_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

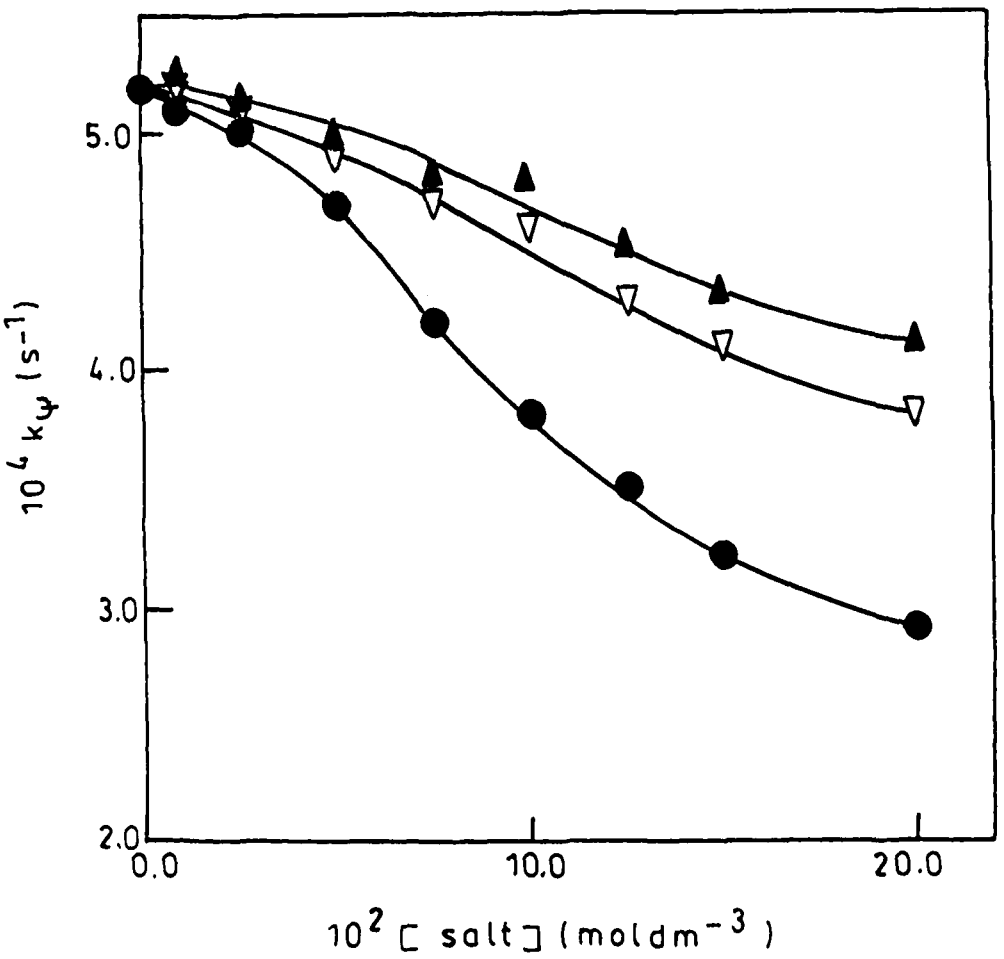


Fig. 3.23: Effect of $[salt]_T$ (Na_2SO_4 (●), $NaNO_3$ (▽) and NaCl (▲)) on the rate of oxidation of D(–)fructose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[D(-)fructose]_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

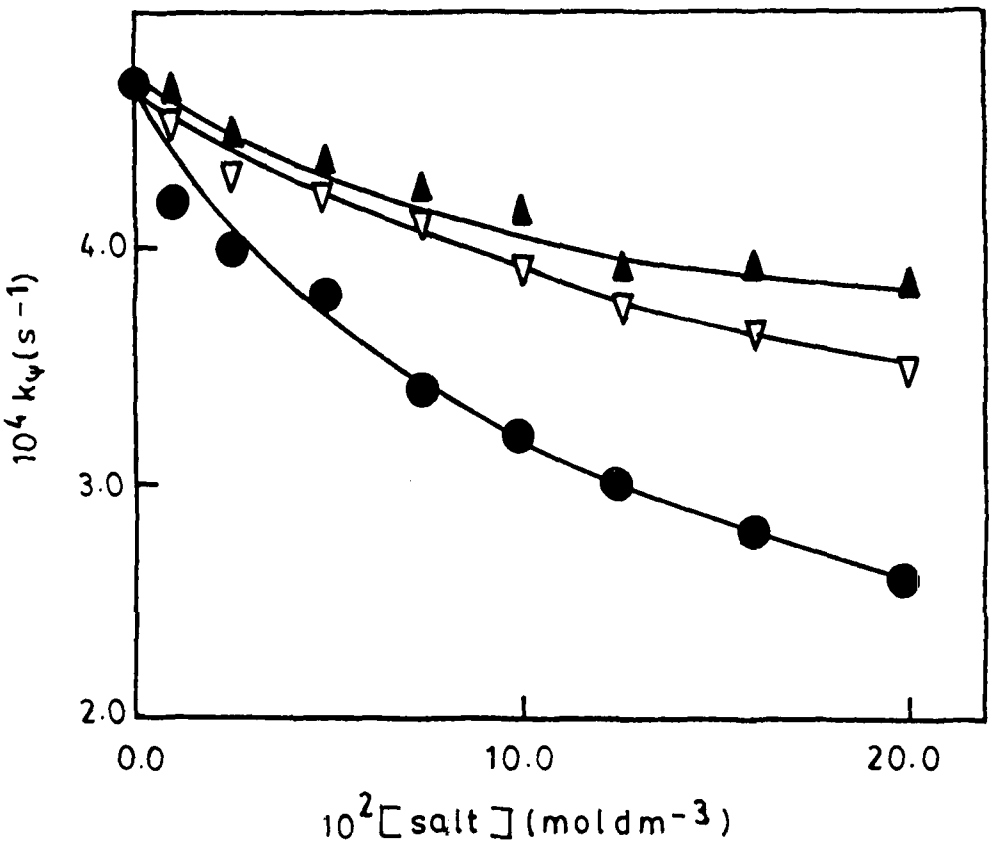


Fig. 3.24: Effect of $[salt]_T$ (Na_2SO_4 (●), $NaNO_3$ (▽) and NaCl (▲)) on the rate of oxidation of L(–)sorbose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, [L(–)sorbose]$_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

B. Discussion

The mechanism

(a) in the absence of CTAB

Evidence for the formation of stable co-ordination complexes has been obtained by kinetic and spectrophotometric methods for cerium(IV) oxidations of many compounds in perchloric and nitric acids.[8,11-13] Complex formation in cerium(IV) oxidations in sulfuric acid solutions, however, has been indicated only in a few studies,[14,15] and in none of these was spectrophotometric evidence provided for the complex. Thus, in aqueous H_2SO_4 media, complexation of organic substrate with Ce(IV)—sulfato species is a rare possibility.[16,17] However, there may be a weak association and the following steps given in Scheme 3.1 are quite reasonable.

$$Ce(IV) + S \underset{}{\overset{K}{\rightleftharpoons}} \text{complex (C)} \qquad (3.3)$$

$$C \xrightarrow{k} Ce(III) + S^{\bullet} + H^{+} \qquad (3.4)$$

$$S^{\bullet} + Ce(IV) \xrightarrow{\text{fast}} \text{products} + Ce(III) + H^{+} \qquad (3.5)$$

Scheme 3.1

The above Scheme is similar to that proposed by Mehrotra *et al.*[18] Here, the complex C unimolecularly disproportionates in the rate determining step to give Ce(III) and free radical $S^{\bullet}$.

A second mechanism assumes that the substrate is directly oxidized by Ce(IV) in a bimolecular step. In this case, the interaction may occur at the transition state (Scheme 3.2).

$$Ce(IV) + S \longrightarrow \{Ce(IV)..... S\} \longrightarrow Ce(III) + S^{\bullet} + H^{+} \qquad (3.6)$$

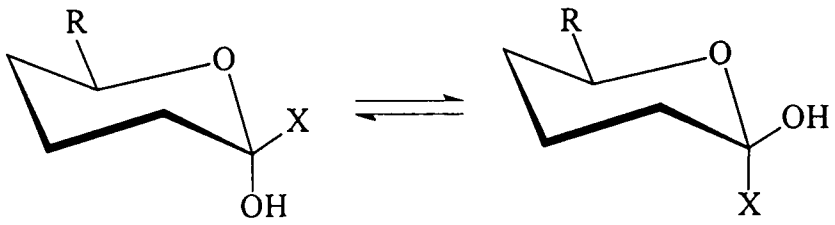
Scheme 3.2

When the K–value is very small then it is not possible to discriminate between Schemes 3.1 and 3.2. In the above Schemes, Ce(IV) actually denotes the kinetically active Ce(IV)–species.

Active species of reductant

Monosaccharides, especially those with five and six carbon atoms, normally exist as cyclic molecules rather than as the open-chain forms. The cyclization takes place as a result of interaction between the functional groups on distant carbons to form a cyclic hemiacetal (in aldoses) or a cyclic hemiketal (in ketoses). In either case, the carbonyl carbon becomes a new chiral center called the anomeric carbon. The cyclic sugar can take either of two different forms, designated α and β, called anomers of each other. A five-membered ring is called a furanose because of its resemblance to furan; a six-membered ring is called pyranose because of its resemblance to pyran. The pyranoid form is generally the most stable and exists mainly as a chair form. Out of these, only the pyranoid form is claimed to be involved in the oxidation reactions.[19] The β–form having

—OH group at C-1 at the equatorial position is more reactive than the α–form (—OH axial).[20]



(α–anomer) (β–anomer)

R = —H (for aldopentoses and ketohexoses) or

—CH_2OH (for aldohexoses)

X = — H (for aldopentoses and aldohexoses) or

—CH_2OH (for ketohexoses)

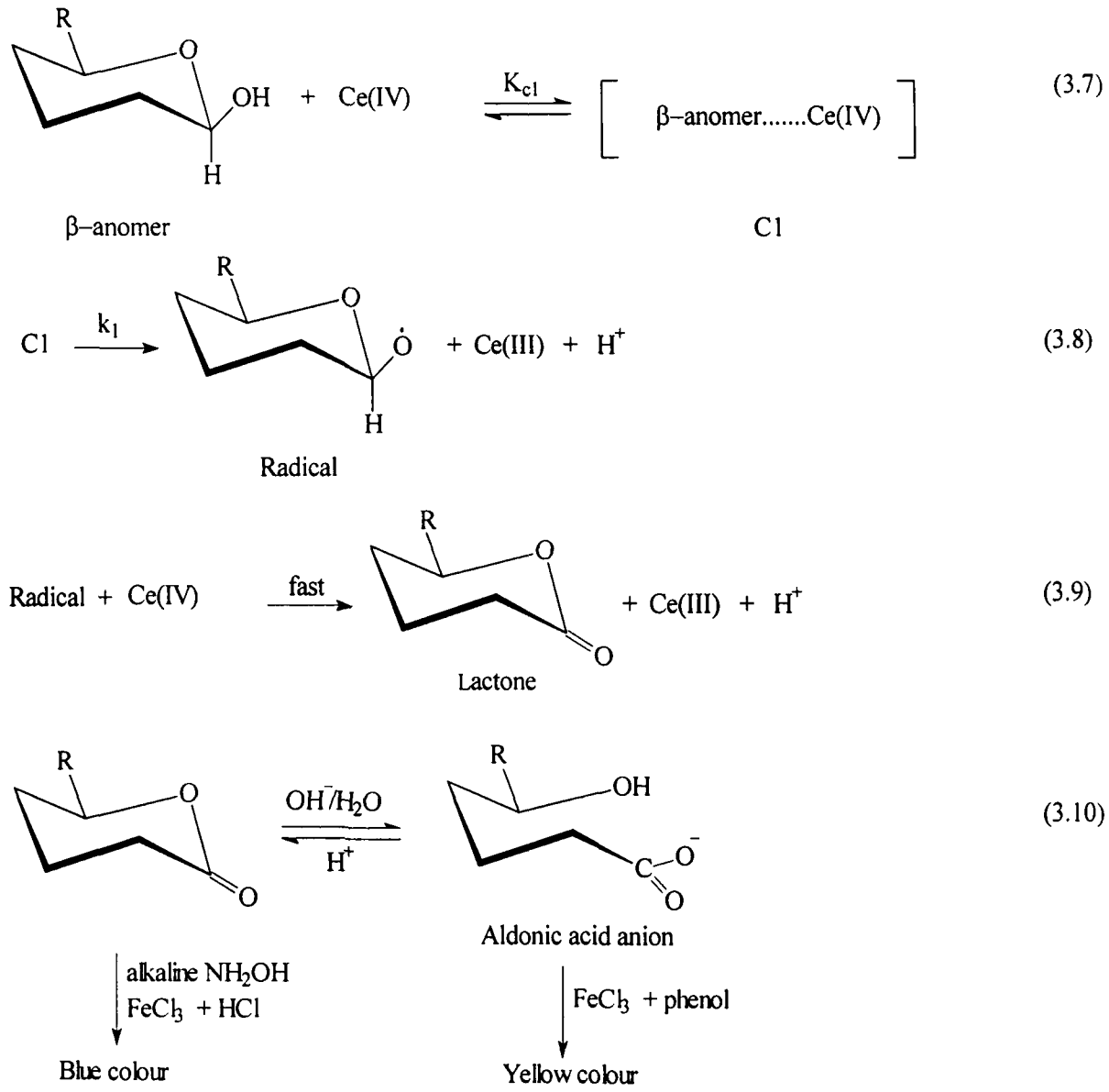
Active species of oxidant

Cerium(IV) oxidations in perchloric acid are generally fast whereas the sulfuric acid medium has been widely used to investigate the reaction with organic substrates, where the ceric species acts as an one-electron oxidant. The primary products of such reactions are radicals which subsequently undergo rapid oxidation to stable species. It is well known that different types of complexes $CeSO_4^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_3^{2-}$, $H_3Ce(SO_4)_4^-$, $HCe(SO_4)_3^-$, and $Ce(OH)^{3+}$ are present in a ceric sulfate solution and that their relative concentration is a function of the pH and sulfate ion concentration.[6,21-24]

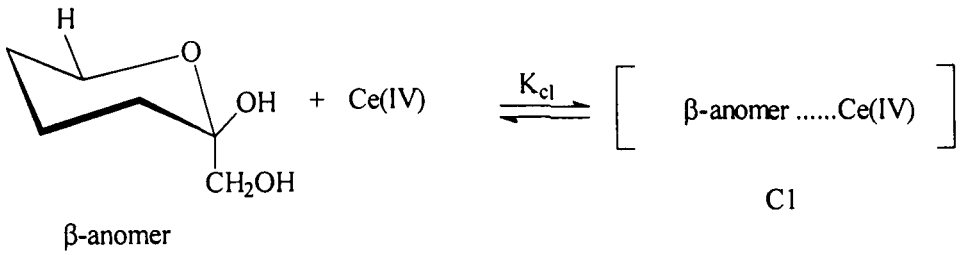
On the basis of rate inhibitory effects of H_2SO_4 and HSO_4^-, $Ce(SO_4)_2$ has been considered to be the reactive form.[23,25,26] On the other hand, HSO_4^- and H_2SO_4 dependencies also suggest the participation of $HCe(SO_4)_3^-$ and $H_3Ce(SO_4)_4^-$, respectively,[26,27] as the reactive cerium(IV) species. In our study, the reaction is catalyzed by CTAB while anionic SDS has no effect. This clearly indicates the involvement of a negatively charged species of cerium(IV) and excludes the possibility of $Ce(SO_4)_2$ being the reactive species (attraction and repulsion, respectively, between the negatively charged cerium(IV) species and the head groups of the two types of surfactant micelles seemingly play important role in the present case). Thus, it may be considered that $Ce(SO_4)_3^{2-}$, $HCe(SO_4)_3^-$, and $H_3Ce(SO_4)_4^-$ could be the reactive species in the present systems, but, the dependency on $[H_2SO_4]$ (inverse-order) indicates that $H_3Ce(SO_4)_4^-$ can not be the active form. Previous observation of Hardwick and Robertson[6] suggested that *ca.* 93% of the cerium(IV) in 1N H_2SO_4 is present as $Ce(SO_4)_3^{2-}$ and proposed the equilibrium $Ce(SO_4)_2 + HSO_4^- \rightleftharpoons Ce(SO_4)_3^{2-} + H^+$ but the formation of $Ce(SO_4)_3^{2-}$ has been questioned.[21,22] For argument sake, if we do consider $Ce(SO_4)_3^{2-}$ as the reactive species, simultaneous formation of $HCe(SO_4)_3^-$ is equivalent to the formation of $Ce(SO_4)_3^{2-} + H^+$ in solution. Presently, it is difficult to answer as which of the two negatively charged species ($Ce(SO_4)_3^{2-}$ or $HCe(SO_4)_3^-$) is the active form of cerium(IV) (also, at $[H_2SO_4]$ = 1.83 mol dm^{-3}, the fractions of these species are high: 2.46×10^{-7} (Ce^{4+}), 4.71×10^{-4} ($CeSO_4^{2+}$), 0.051 ($Ce(SO_4)_2$), 0.562 ($Ce(SO_4)_3^{2-}$), 0.184 ($HCe(SO_4)_3^-$), 0.201 ($H_3Ce(SO_4)_4^-$)).

On the basis of observed results (first-order with respect to oxidant and reductant) and these arguments, a general mechanistic scheme may be proposed depicting the behavior of carbohydrates towards the oxidant cerium(IV).

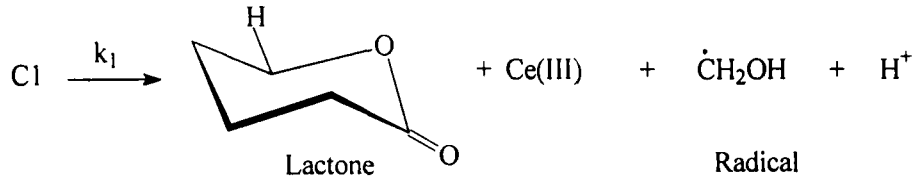
Schemes 3.3 and 3.4 explain, respectively, the oxidation of aldoses and ketoses.



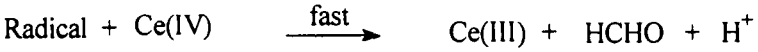
Scheme 3.3



(3.11)



(3.12)



(3.13)

Scheme 3.4

The first step in Scheme 3.3 is the complex formation between the reactive species of cerium(IV) and β-anomer. The redox decomposition of this complex C1 in the subsequent rate-determining step gives rise to free radical and Ce(III) (Eq. (3.8)). The lactones are the oxidation products of aldoses in accordance with Eq. (3.9).

In the oxidation of ketoses (Scheme 3.4), the first step is same as that in case of aldoses, *i.e.*, the formation of a complex. The second step is the rate determining step leading to the formation of lactone, free radical and Ce(III). The free radical combines with Ce(IV) to produce Ce(III) and formaldehyde.

The rate determining steps in both the Schemes 3.3 and 3.4 are similar. Therefore, the rate law for both aldoses and ketoses should also be similar which can be given as

$$\frac{-d[Ce(IV)]}{dt} = k_1 K_{c1}[\text{carbohydrate}]\,[Ce(IV)] \qquad (3.14)$$

The rate law (Eq. (3.14)) is in complete accord with the observations, *i.e.*, first-order dependence both in [carbohydrate] and [Ce(IV)] (as explained above, exact equation for observing the inverse-order kinetics each in $[H_2SO_4]$ and $[HSO_4^-]$ cannot be derived due to uncertainty of the involved protonic equilibria producing the active Ce(IV) species).

The oxidation kinetics of carbohydrates by cerium(IV) proceed in two stages, *i.e.*, initial slow stage followed by a relatively faster step. The mechanism of first step is discussed here. The second step oxidation (autocatalytic reaction path) is not a true reaction path for the oxidation of carbohydrates by cerium(IV): it may be a mixture of the rates of carbohydrates and their oxidation products (lactones and aldonic acids). Sala and coworkers studied the oxidation of lactones by chromium(VI) and reported that the rates of their oxidation are at least 10-fold higher in comparison to corresponding monosaccharides.[28,29] Thus, it can be concluded that under the present kinetic conditions, the exact stoichiometry and product analysis cannot be predicted and the exact dependence of the autocatalysis path on reactant concentrations cannot be estimated.

(b) in the presence of CTAB

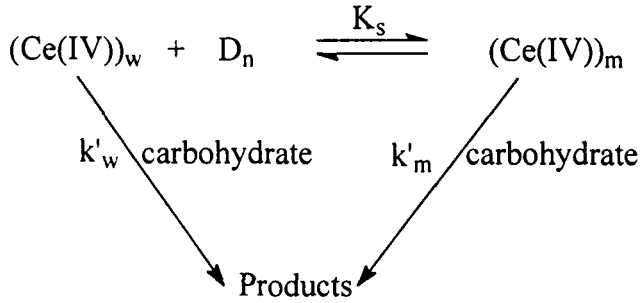
Micellar aggregates composed of single chain surfactant molecules are the simplest of the dynamic aggregates to affect catalysis. There are numerous reactions in which solubilization of one or more of the reactants in the micellar aggregates leads to significant alteration in the reaction rates. Solubilization introduces two new situations that can influence the reaction rates: alteration in the local distribution of the solute (reactants) and surface/interface effects.

It has already been mentioned that the reactions of cerium(IV) and carbohydrates are catalyzed by cationic micelles of CTAB while anionic micelles of SDS have no effect on the rates. The dependencies on variables like [reductant], [oxidant], $[H_2SO_4]$, and temperature are same both in aqueous and CTAB media. Therefore, it can be concluded that the mechanisms of redox reactions of cerium(IV) and carbohydrates remain the same in both the media.

Lower values of activation energy in presence of CTAB as compared to reactions in aqueous medium (Tables 3.25–3.30) clearly indicate that the CTAB acts as catalyst and provides a new reaction path with lower activation energies. However, a complete account of all the factors that influence $\Delta H^{\#}$ and $\Delta S^{\#}$ is not possible because the rate constant k_{Ψ} does not represent a single elementary step (as it being a complex function of k'_w, k'_m, and K_s, Scheme 3.5). Furthermore, though a change in temperature is known to produce changes in size, shape, surface charge, *etc.* of the micelles, equally good fit of the observed data (k_{obs}

and k_Ψ) to the Eyring equation both in the absence as well as presence of surfactants shows that the micelle structural sensitivity to temperature is kinetically unimportant. Similar conclusions had been drawn earlier also.[30,31]

The kinetic results of the effect of varying [CTAB] on the rates of reactions can be explained by means of pseudophase model proposed by Menger and Portnoy,[32] which takes into consideration solubilization of one reactant only into the micellar phase. The variation of rate constants with surfactant concentration is treated on the assumption that the substrate (the kinetically active Ce(IV)–species) is distributed between the aqueous and micellar pseudophases as given in Scheme 3.5 ($(Ce(IV))_m$ is the micellized Ce(IV)–species, $[D_n] = [surfactant]_T - cmc$, K_s is the micelle—Ce(IV) binding constant and k'_w and k'_m are the respective first-order rate constants in aqueous and micellar pseudophases).



Scheme 3.5

According to Scheme 3.5, the observed rate constant is expressed as a function of $[D_n]$, Eq. (3.15),[32]

$$k_\psi = \frac{k'_w + k'_m K_s [D_n]}{1 + K_s [D_n]} \qquad (3.15)$$

On rearranging, Eq. (3.15) gives Eq. (3.16)

$$\frac{1}{(k'_w - k_\psi)} = \frac{1}{(k'_w - k'_m)} + \frac{1}{(k'_w - k'_m) K_s [D_n]} \qquad (3.16)$$

Equation (3.16) predicts that a plot of left-hand side *versus* $[D_n]^{-1}$ should be linear. When the data were fitted into Eq. (3.16), good linear plots were observed (Figs. 3.25–3.30) implying that the Scheme 3.5 model is suitable to explain the observed catalytic role of CTAB micelles. The values of K_s and k'_m were calculated for each carbohydrate from the slopes and intercepts of the respective plots of $1/(k'_w - k_\psi)$ *versus* $1/[D_n]$. These values are given in Table 3.43. K_s, k'_m and $[D_n]$ were used to recalculate rates ($k_{\psi cal}$, Tables 3.31–3.36) which are in good agreement with the observed k_ψ; this confirms the validity of rate law Eq. (3.15) and the Scheme 3.5 model.

Probable reaction site

All micellar-mediated reactions are concluded to occur in the Stern layer.[33] Micellar surfaces are water rich[34] (activity of the water at the surfaces of ionic micelles is not different from water activity in the aqueous pseudophase). Electrostatic and hydrophobic interactions play important role in the

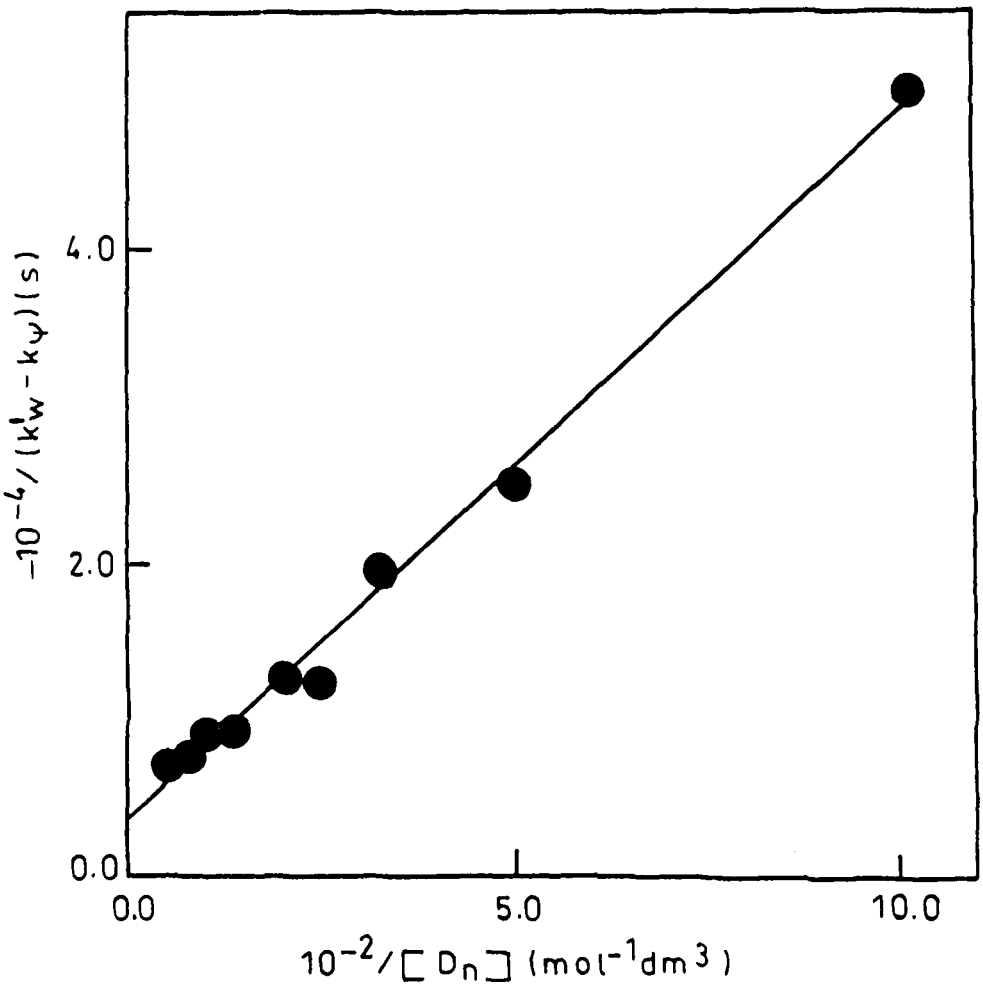


Fig. 3.25: Plot of $1/(k'_w - k_\psi)$ *versus* $1/[D_n]$ for the oxidation of D(+)xylose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[D(+)xylose]_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

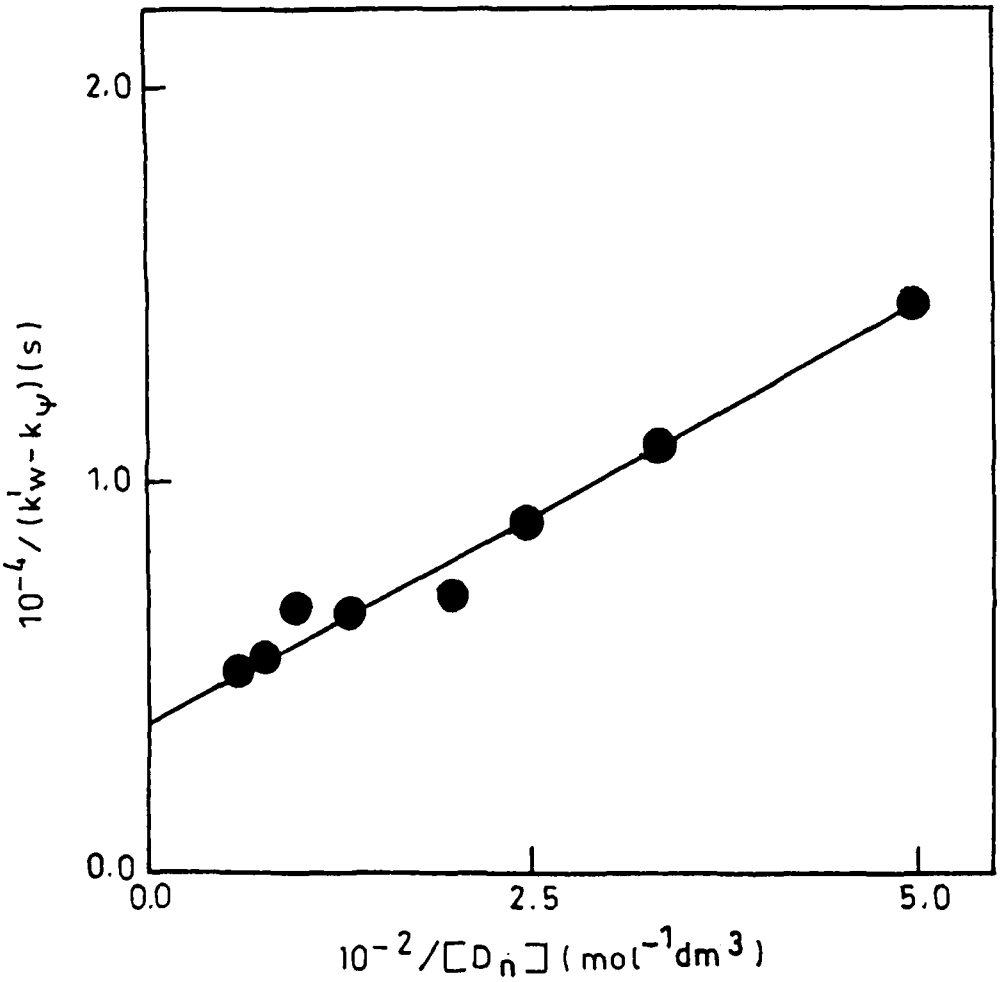


Fig. 3.26: Plot of $1/(k'_w - k_\psi)$ *versus* $1/[D_n]$ for the oxidation of L(+)arabinose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[L(+)arabinose]_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

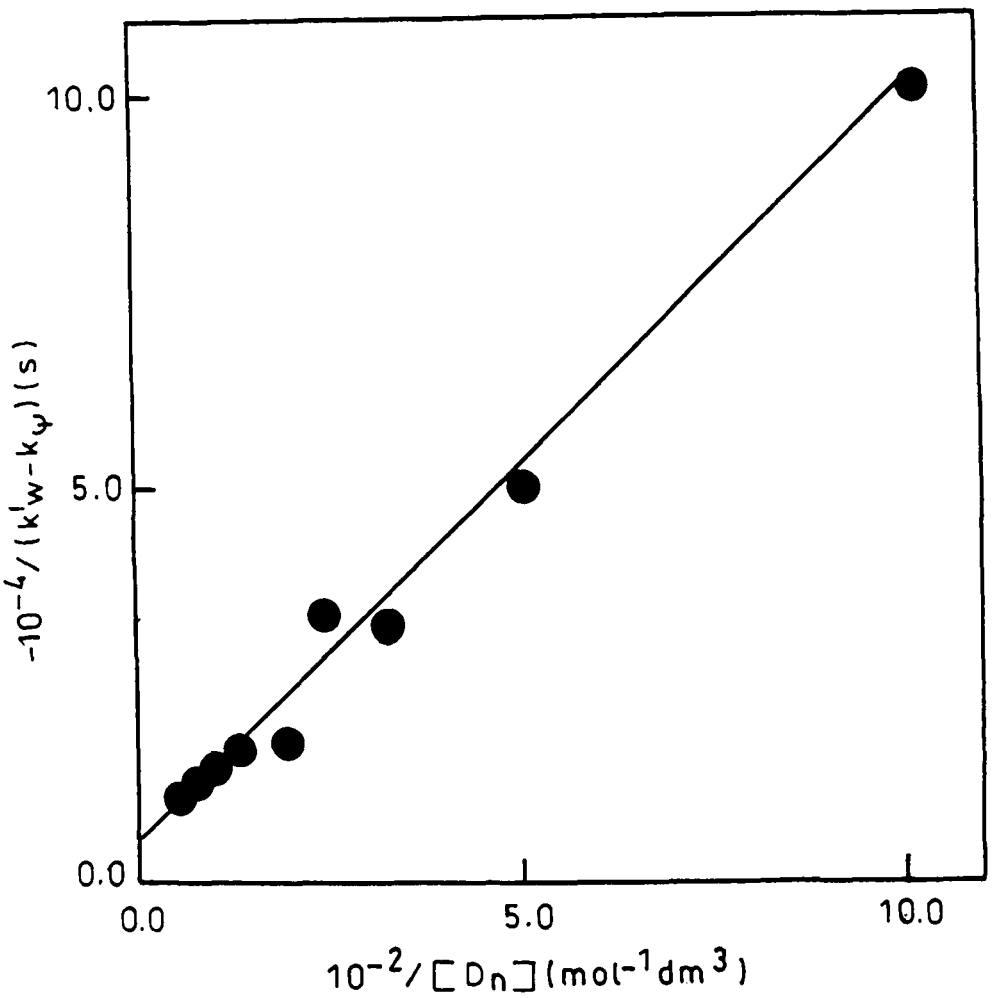


Fig. 3.27: Plot of $1/(k'_w - k_\psi)$ *versus* $1/[D_n]$ for the oxidation of D(+)glucose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[D(+)glucose]_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

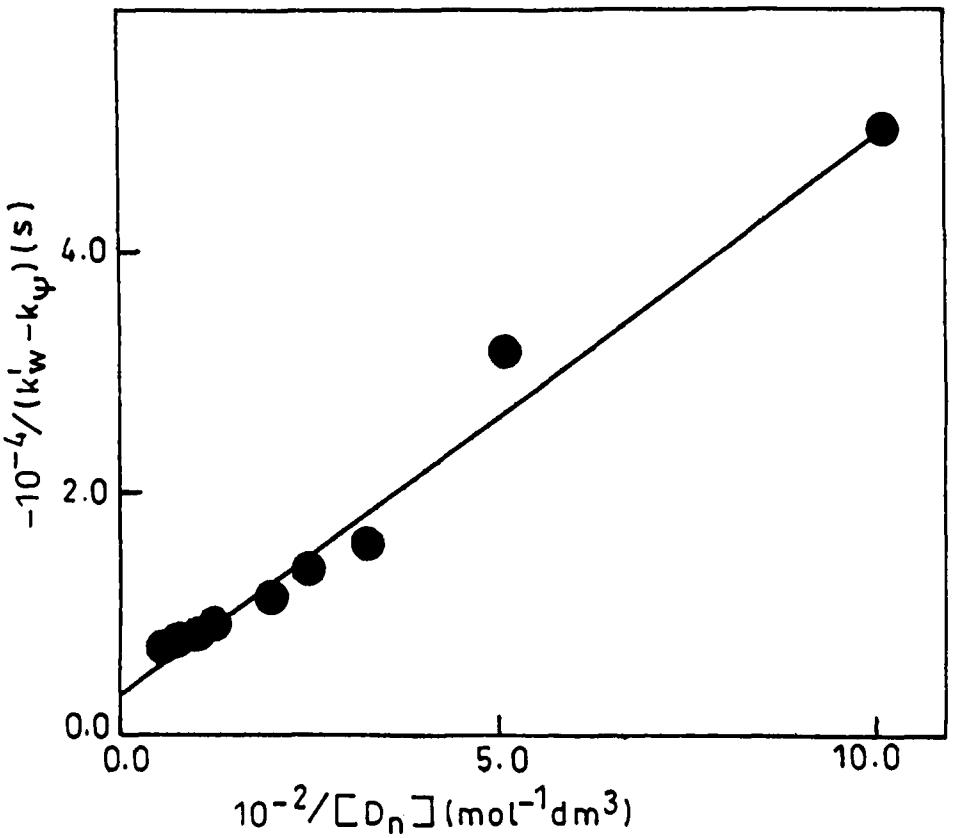


Fig. 3.28: Plot of $1/(k'_w - k_\psi)$ *versus* $1/[D_n]$ for the oxidation of D(+)mannose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[D(+)mannose]_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

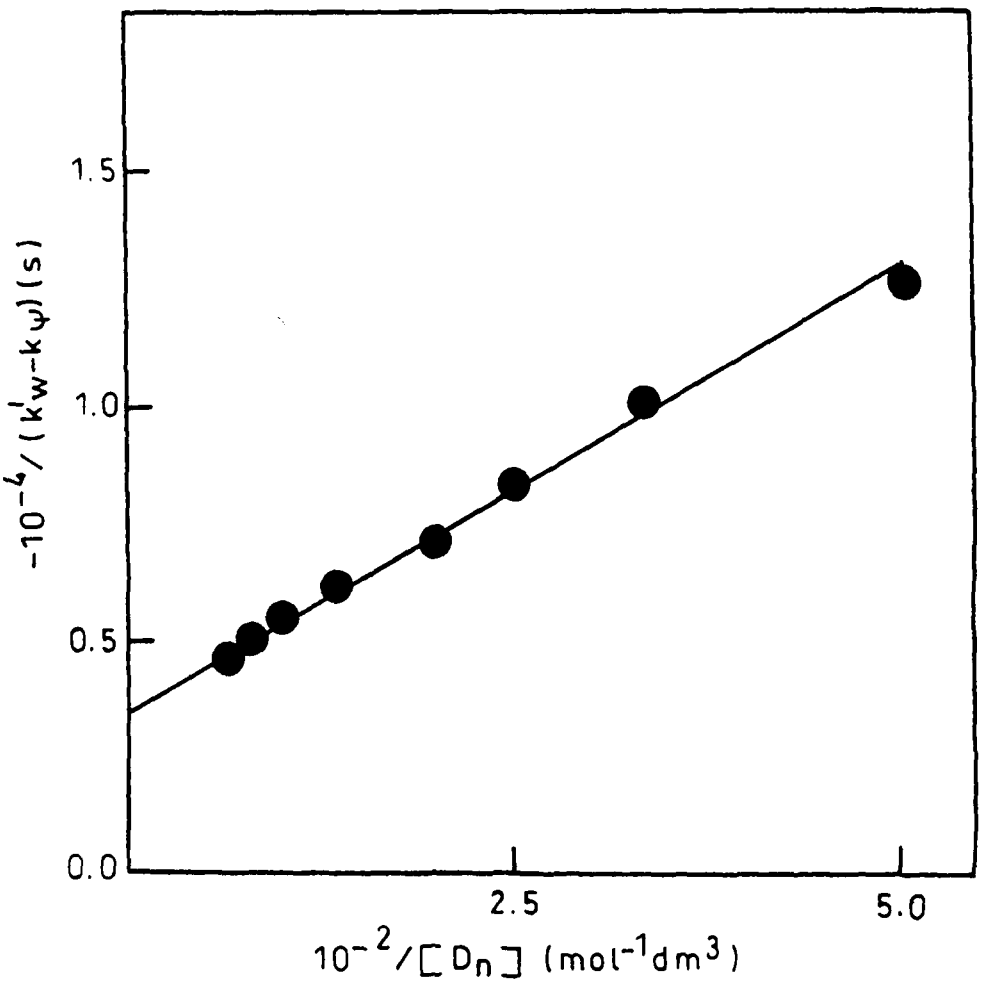


Fig. 3.29: Plot of $1/(k'_w - k_\psi)$ *versus* $1/[D_n]$ for the oxidation of D(–)fructose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, $[D(-)fructose]_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

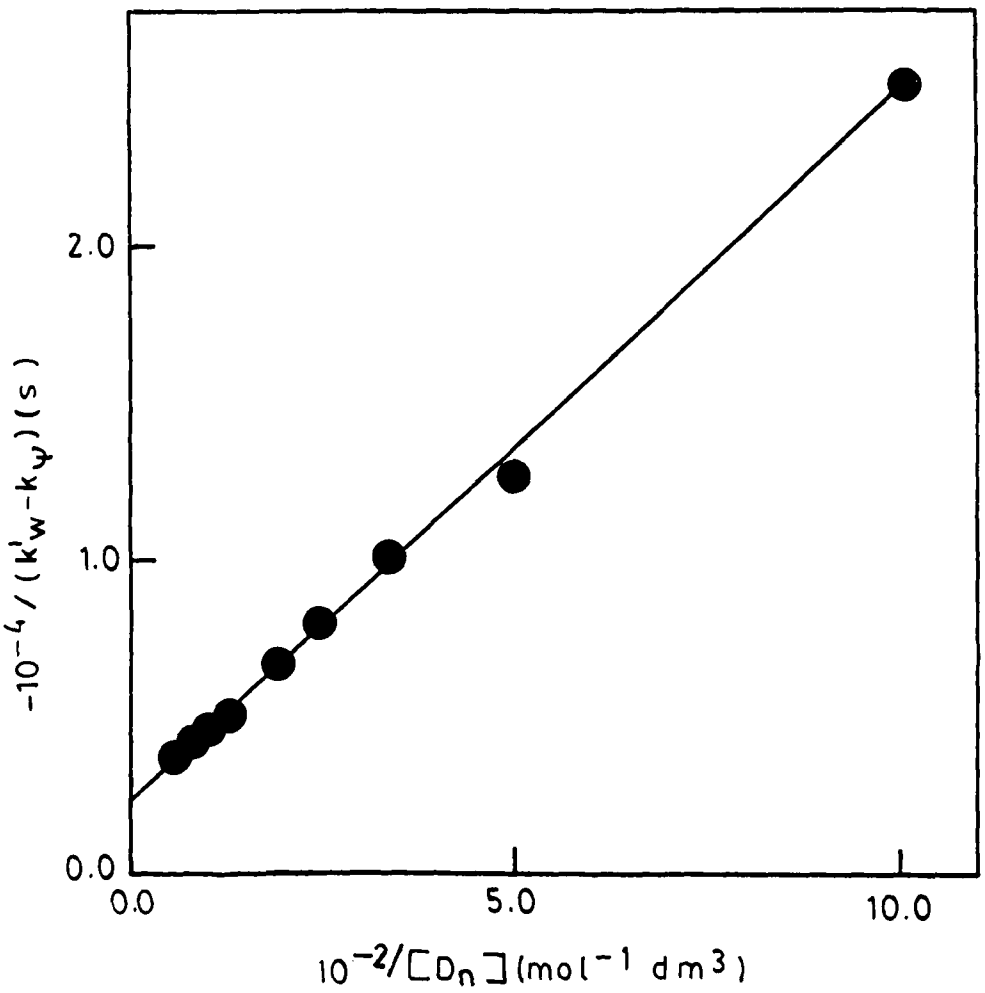


Fig. 3.30: Plot of $1/(k'_w - k_\psi)$ *versus* $1/[D_n]$ for the oxidation of L(–)sorbose by cerium(IV) in presence of CTAB (= 50.0 x 10^{-3} mol dm^{-3}). *Conditions:* $[Ce(IV)]_T$ = 1.0 x 10^{-3} mol dm^{-3}, [L(–)sorbose]$_T$ = 4.0 x 10^{-2} mol dm^{-3}, $[H_2SO_4]_T$ = 1.83 mol dm^{-3}, temperature = 40 °C.

TABLE 3.43:

Values of micelle–cerium(IV) binding constants (K_s) and rate constants in micellar medium (k'_m) for the oxidation of carbohydrates by cerium(IV) in presence of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}
$[carbohydrate]_T$ = 4.0×10^{-2} mol dm^{-3}
$[H_2SO_4]_T$ = 1.83 mol dm^{-3}
Temperature = 40 °C

Carbohydrate	K_s (mol^{-1} dm^3)	10^4 k'_w[a] (s^{-1})	10^4 k'_m (s^{-1})
D(+)xylose	89.0	1.7	4.2
L(+)arabinose	165.3	2.2	5.0
D(+)glucose	52.1	1.1	3.1
D(+)mannose	58.2	1.5	4.8
D(–)fructose	191.0	3.8	6.6
L(–)sorbose	99.9	3.2	7.6

[a] $k'_w = k_{obs}$, obtained under similar conditions without added CTAB (see Tables 3.1–3.6)

incorporation/association of substrates into micelles. Many ionic species of cerium(IV) are believed to be present in the aqueous H_2SO_4 medium.[6,21,35–37] The positive catalytic effect of CTAB micelles indicates that the chemically active species must be anionic which may get associated through electrostatic interaction with the positive head group of CTAB micelles. The second reactant, carbohydrate, has no hydrophobicity due to the presence of 4 or 5 hydrophilic —OH groups. As the reaction proceeds through the formation of a complex (see Eq. (3.7)/(3.11)), the associated Ce(IV)–species may form complex C_1 at the Stern and Gouy-Chapman layers' junctural region[38–43] (see Fig. 3.31 of a possible arrangement). The complex, having negative charge, may now orient in a manner suitable for proceeding the reaction further.

Effect of SDS micelles

It is evident from the data depicted in Tables 3.31–3.36 and Figs. 3.13–3.18 that SDS has no effect on the reaction rate. The negative head groups of SDS micelle simply repel the anionic species of cerium(IV). On the basis of these observations our conclusion that, out of various sulfate species of cerium(IV), only those with negative charge are the reactive species seems logical.

Effect of [salt] on the k_Ψ

When salts are added to micellar solutions, the counterions of the salts compete for the ionic head group of micelles with the surfactant counterions

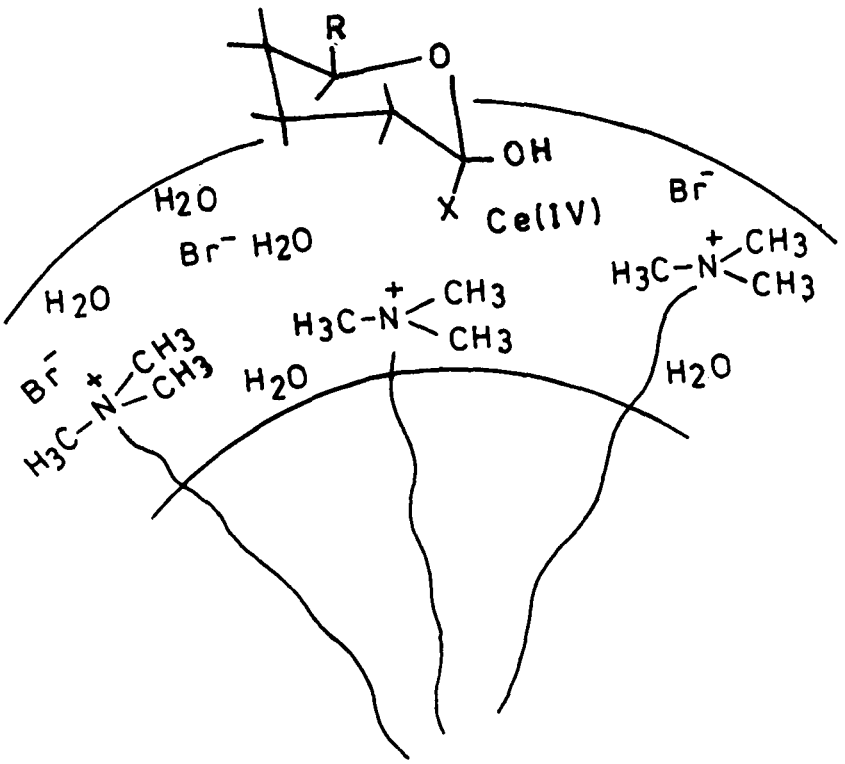


Fig. 3.31: Schematic model showing probable location of reactants for the ionic micellar catalyzed redox reaction between cerium(IV) and carbohydrates.

that already exist in solution. Thus, displacement can occur, depending on the relative affinities of counterions for the head groups. Kinetic salt effects are peculiar in micellar systems[44] and interesting kinetic effects can arise. If the added salt is reactive, micellar rate enhancements are observed after displacement. Inert salts, especially the inorganic ones, and organic additives have generally been found to decrease the rates of reactions.

The salt effects are specific and depend upon the nature of the ion which has a charge opposite to that of the micelle, suggesting that both electrostatic and hydrophobic factors play a role. The effects are greatest for large, low charge density and hydrophobic ions which interact most strongly with the reactive counterionic micelles. In general, the more hydrophobic a character possessed by the ion, the better inhibitor it becomes. The inhibitory effect of an ion increases with its ability to lower the critical micelle concentration and surface potential, to increase aggregation number, and to decrease the ionization degree of micelles.[45–47]

It has been reported that upon the addition of salts or organic solvents, micellar surfaces become more hydrated and the water content of the micellar interface plays an important role in inhibition.[48,49]

Our results of the effect of inorganic electrolytes (NaCl, $NaNO_3$ and Na_2SO_4) on the CTAB-catalyzed oxidation of carbohydrates by cerium(IV) show that the added salts inhibit the rates of reactions (Tables 3.37–3.42 and Figs. 3.19–3.24). Each anion is an inhibitor and the inhibitory power increases in the

order: $Cl^- < NO_3^- < SO_4^{2-}$. As the concentration of these electrolytes increases, the concentration of Ce(IV) at the reaction site decreases (the counterions of the added salts compete with the reactive Ce(IV)–species for the CTAB head group region). Our kinetic salt effects thus suggest that some additional factors than changes in micellar size and shape are involved in the present system. The inhibitory effect may thus, at least in part, be due to the exclusion of reactive species of cerium(IV) from the reaction site.

Comparison of second-order rate constants

Table 3.44 summarizes the values of second-order rate constants (k^{II}, mol^{-1} dm^3 s^{-1}) for the reactivity of carbohydrates, used in this study, with cerium(IV). These results indicate that presence of —OH, —CHO and ketonic groups increase the reducing power in the order aldohexoses < aldopentoses < ketohexoses. The trend shows that the oxidation by cerium(IV) seemingly depends on the number of —OH groups, stereochemistry and the chelating ability of the monosaccharides. D(–)fructose has greater tendency to reduce cerium(IV) in comparison to L-sorbose and other monosaccharides (L(–)sorbose > L(+)arabinose > D(+)xylose > D(+)mannose > D(+)glucose). It is interesting to note that the oxidation rate of various monosaccharides studied are of the same order. This means that these sugars are oxidized by a common mechanism, *i.e.*, cerium forming a complex with C-1 hydroxyl group of the sugar prior to its rate-limiting disproportionation to a free radical.

TABLE 3.44

Second-order rate constants for the oxidation of carbohydrates by cerium(IV) in absence (k^{II}) and presence (k_{Ψ}^{II}) of CTAB.

Conditions: $[Ce(IV)]_T$ = 1.0×10^{-3} mol dm^{-3}

$[carbohydrate]_T$ = 4.0×10^{-2} mol dm^{-3}

$[H_2SO_4]_T$ = 1.83 mol dm^{-3}

Temperature = 40 °C

Carbohydrate	$10^3 k^{II} / k^{II}_{\Psi}$ ($mol^{-1}dm^3s^{-1}$)	
	Aqueous	CTAB[a]
D(+)xylose	4.2	6.3
L(+)arabinose	5.5	9.5
D(+)glucose	2.8	4.3
D(+)mannose	3.8	6.0
D(–)fructose	9.5	13.0
L(–)sorbose	8.0	11.8

[a]$[CTAB]_T$ = 50.0×10^{-4} mol dm^{-3}

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